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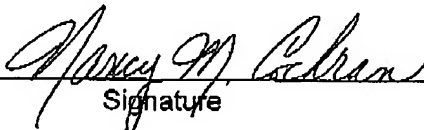
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10/539718  
CH2883USPCT

APPEAL BRIEF UNDER 37 CFR 41.37 (23 pages)

## REFERENCES FOR EVIDENCE APPENDIX:

U.S. Patent No. 4,246,022 (5 pages)  
Great Britain Patent No. 744,074 (3 pages)  
Australian Patent No. 219,385 (3 pages)  
U.S. Published Patent Application No. 2001/0016182 (8 pages)  
U.S. Patent No. 2,600,881 (4 pages)  
U.S. Patent No. 2,592,021 (6 pages)  
Ex parte Rubin 128 USPQ 440 (Pat. Office Bd. of App. 1959) (3 pages)  
In re Burhans 69 USPQ 330 (CCPA 1946) (3 pages)Page 1 of 52

This collection of information is required by 37 CFR 1.8. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1.8 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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PATENT

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

IN THE APPLICATION OF:

Cronin et al.

CASE NO.: CH2883 US PCT

APPLICATION NO.: 10/539,718

GROUP ART UNIT: 1793

FILED: JULY 20, 2005

EXAMINER: NGUYEN, NGOC YEN M

FOR: PURIFICATION OF TITANIUM TETRACHLORIDE

**APPEAL BRIEF UNDER 37 CFR § 41.37**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

In accordance with the practice under 37 CFR 41.37, the following is a brief in support of the Appeal filed February 29, 2008, appealing the Rejection dated December 31, 2007.

Please charge any necessary fees associated with the Appeal Brief pursuant to 37 CFR § 41.20(b) (2), to Deposit Account No. 04-1928 (E. I. du Pont de Nemours and Company). The Commissioner is hereby authorized to charge any additional fees which may be required or credit any overpayment to Deposit Account No. 04-1928.

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US Patent No. 2,595,021.....	6 pages
Ex parte Rubin 128 USPQ (Pat. Office Bd. Of App. 1959).....	3 pages
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**(I) REAL PARTY IN INTEREST**

The real party in interest is E. I. DuPont de Nemours & Co., Inc., a corporation of Delaware, the assignee of this application.

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**(ii) RELATED APPEALS AND INTERFERENCES**

There are no related appeals and/or interferences known to  
Applicants.

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**(iii)STATUS OF CLAIMS**

Claims 1-11 were in the application as filed. Claims 1-11 were rejected by Office Action of March 24, 2006. Claims 1-11 were cancelled. Claims 12-19 were presented in an Amendment on November 6, 2006. The claims were entered by the Examiner. Claims 12-19 were finally rejected by Office Action of December 31, 2007.

Claims 12-19 are on appeal. All claims are rejected. Claims on appeal are listed in the Appendix hereto.

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(iv) **STATUS OF AMENDMENTS**

There has been one amendment to the claims after final rejection which was filed on March 25, 2008 to place the claims in better form for consideration on appeal by correcting a typographical error in claims 1 and 19. In claim 1 subparagraph "(c)" should be corrected to read in proper sequence as subparagraph "(b)". In claim 19 subparagraph "(c)" should be corrected to read subparagraph "(a)". The status of the Amendment After Final is unknown to appellant. The claims presented in this Brief are as amended prior to the Amendment After Final since the Amendment After Final is not considered to touch the merits of the application or raise any issues of substance.

**(v) SUMMARY OF CLAIMED SUBJECT MATTER**

There is one independent claim, claim 12, which claims:

An improved process for purifying a crude titanium tetrachloride chlorinator discharge from the carbo chlorination of titanium-containing materials comprising titanium tetrachloride, aluminum chloride and vanadium chlorides, by mixing a vanadium passivating agent selected from the group consisting of organic oil into the chlorinator discharge to form a passivated discharge comprising one or more easy-to-separate vanadium-containing compounds, wherein the improvement comprises:

- (a) detecting, in the passivated discharge, titanium oxychloride formed therein, and, if titanium oxychloride is absent, missing an aluminum passivating agent into the passivated discharge in an amount sufficient to passivate the aluminum chloride and react with the titanium tetrachloride to form titanium oxychloride, the aluminum passivating agent being selected from the group consisting of water, water containing solutions, water containing mixtures, and carboxylic acid to form one or more easy-to-separate aluminum-containing compounds in the passivated discharge; and
- (c) separating from the passivated discharge the easy-to-separate vanadium- and aluminum-containing compounds to form a purified titanium tetrachloride.

The dependent claims add various other limitations, such as particular separation processes, an amount of vanadium passivating agent sufficient to reduce the concentration of, but not eliminate, the vanadium chlorides, a particular purge-containing product as the aluminum passivating agent, a process control method for controlling mixing the passivating agents, particular vanadium passivating agents, and a second amount of vanadium passivating agent mixed into the passivated discharge.



The locations of these various features in the specification of the application are given below by the number of the claim in which they are recited.

12. Page 3, line 10 to page 4, line 5, line 29 to page 5, line 2 and lines 9-34, page 6 lines 2-9, page 7, lines 17-23, page 8, line 27- page 9, line 2, also see Examples 1 and 2 and proviso (ii) of original claim 1.
13. Page 4, lines 8-11 and original claim 2.
14. Page 4, lines 31-34 and original claim 6.
15. Page 8, lines 7-9 and original claim 7.
16. Page 8, lines 10-26 and original claim 8.
17. Page 6, lines 30-32 and original claim 10.
18. Page 6, lines 32-34 and original claim 11.
19. Page 4, line 29 to page 5, line 8.

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**(vi) GROUND OF REJECTION TO BE REVIEWED ON APPEAL**

Claims 12-19 were rejected under 35 U.S.C. §103(a) as being obvious over the preamble to Jepson claim 12 as admitted prior art ("the preamble") or U.S. Published Patent Application No. 2001/0016182 A1 ("the Cronin et al. publication").

Claims 1-11 were rejected under 35 U.S.C. §103(a) as being obvious over U.S. Patent No. 2,600,881 of Kay et al. ("the '881 patent") in view of U.S. Patent No. 2,592,021 of Frey et al. ("the '021 patent") and the Cronin et al. publication.

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**(vii) ARGUMENT**

**Brief Summary of the Background**

Titanium tetrachloride can be produced by chlorinating a titanium-containing material, typically a titanium-rich ore such as rutile. The raw materials, in addition to containing titanium, contain other metals which can be considered impurities such as vanadium and aluminum among other impurities. The impurities can be chlorinated along with the titanium resulting in a chlorinator discharge which can contain a major proportion of titanium tetrachloride and a minor proportion of chlorinated vanadium and aluminum.

The chlorinated vanadium form yellow colored species which are undesirable, see Great Britain Patent No. 744,074 and also the instant specification at page 2, lines 12-14.

To remove the chlorinated vanadium, U.S. Patent No. 4,246,022 of Robinson teaches purifying the chlorinator discharge by treatment with an organic oil, see Col. 1, lines 9-43. Vanadium chloride resulting from this purification step is a solid which can more easily be separated from the titanium tetrachloride product. This purification step can be referred to as "vanadium passivation". See Australian Patent No. 219,385. Also see the instant specification at page 2, lines 12-19.

The chlorinated aluminum impurities are highly corrosive and they attack the metal materials of construction in the downstream equipment, see the Cronin et al. publication and also the instant specification at page 1, lines 28-32.

To remove the chlorinated aluminum, U.S. Patent No. 2,600,881 of Kay et al. ("the '881 patent") teaches that water can be added to the crude titanium tetrachloride (also known as the chlorinator discharge). The Cronin et al. publication teaches that water can react with the aluminum chloride converting it to a less volatile non-corrosive hydrate or oxychloride. This purification step can be referred to as "aluminum

chloride passivation". See the '881 patent at page 1 [0003] to [00004]. Also see the instant specification at page 2, lines 1-11.

The inventors discovered that a passivating agent for aluminum chloride results from using organic oil for passivation of vanadium oxychloride in the crude titanium tetrachloride chlorinator discharge. From this surprising discovery, an improved process for purifying crude titanium tetrachloride was discovered which can reduce titanium yield loss, improve raw material utilization to reduce process cost and the amount of waste produced. See the instant specification at page 5, lines 27-34. In the improved process, the aluminum chloride passivation, by way of the vanadium passivation using organic oil, is determined by the titanium oxychloride concentration in the vanadium passivated product. When titanium oxychloride is detected in the vanadium passivated product, aluminum chloride has been passivated. However, when titanium oxychloride is absent, the aluminum chloride has not been passivated requiring use of an aluminum passivating agent, see the instant specification at page 6, lines 6-19.

Vanadium passivated titanium tetrachloride streams can contain tenacious solids, as high as 50 to 60%, which are difficult to deal with in the analytical equipment which is needed to detect the presence (or absence) of substances such as titanium oxychloride. As such, the art of vanadium passivated titanium tetrachloride did not lend itself to analyzing vanadium passivated titanium tetrachloride for substances such as titanium oxychloride which lead to the discovery that only if titanium oxychloride is absent in the vanadium passivated titanium tetrachloride stream would it be necessary to use an aluminum chloride passivating agent.

**Rejection under 35 U.S.C. §103(a) in view of the preamble to Jepson claim 12 as admitted prior art ("the preamble") or Great Britain Patent No. 744,074 ("the '074 publication"), either one in view of Cronin et al.**

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**U.S. Published Patent Application No. 2001/0016182 ("the Cronin et al. publication").**

**Claims 12-13 and 15-18**

Claims 12-13 and 15-18 are considered to stand or fall together.

In rejecting claims 12-13 and 15-18, the Examiner found that the preamble of the Jepson-style claim presented is admitted prior art and that the admitted prior art or the '074 publication can be pointed to for disclosing a process for purifying titanium chloride to passivate vanadium using an organic oil, in the case of the preamble, or animal wax in the case of the '074 publication. From these citations, the Examiner concludes that it would have been obvious to one of ordinary skill in the art to "...select a known and conventional oil or animal fat in the art to effectively remove the impurities, especially vanadium and/or aluminum from titanium tetrachloride through routine experimentation." The Cronin et al. publication was then relied on for disclosing techniques for passivating aluminum chloride by monitoring titanium oxychloride.

This basis for the conclusion of prima facie obviousness is in error because it ignores an important process step of the claims which is not disclosed in the cited references and would not have been an obvious modification of the teachings of the cited references. While using organic oil or animal wax in processes for removing vanadium was known, using organic oil or animal wax in such processes was not known for removing aluminum and, thus, the process for purifying a crude titanium tetrachloride chlorinator discharge by the process steps of detecting if titanium oxychloride is absent and mixing an aluminum passivating agent into the vanadium passivated discharge in an amount sufficient to passivate the aluminum chloride and react with the titanium tetrachloride to form titanium oxychloride would not have been obvious. Routine experimentation of treatment for removing vanadium chlorides would not have revealed passivating aluminum in titanium tetrachloride chlorinator discharge and further would not have also revealed or suggested that it would have been obvious to detect if titanium oxychloride is absent and mixing an aluminum passivating agent into the passivated discharge in an amount sufficient to passivate the aluminum and react with the titanium tetrachloride to form titanium oxychloride.

Nonobviousness of the claimed process is especially apparent because it was not known that a passivating agent for aluminum chloride is a product that results from using organic oil for passivation of vanadium in the crude titanium tetrachloride discharge. From this surprising discovery, the claimed improved process for purifying crude titanium tetrachloride was discovered which can reduce titanium yield loss, improve raw material utilization to reduce process cost and the amount of waste. See the specification at page 5, lines 27-34. In the improved process, the aluminum chloride passivation, by way of the vanadium oxychloride passivation using organic oil, is determined by the titanium oxychloride concentration in the vanadium passivated product. When titanium oxychloride is detected in the vanadium passivated product, aluminum chloride has been completely passivated. However, when titanium oxychloride is absent, the aluminum chloride has not been completely passivated requiring use of an aluminum passivating agent, see the specification at page 6, lines 6-19.

In responding to the argument that the Cronin publication would not have been obvious to combine with prior disclosures of vanadium passivation, the Office action provides that the Cronin publication teaches the need and the process for passivating aluminum and that the concentration of titanium oxychloride in the chlorinator discharge could be measured in-process to adjust the rate of addition of aluminum chloride passivating agent. However, it is important to note that the claimed feature of detecting the titanium oxychloride concentration is in the vanadium passivated discharge, not the aluminum passivated discharge as taught in the Cronin et al. publication. A person of ordinary skill in the art of crude titanium tetrachloride passivation would not have even considered trying to analyze the vanadium passivated titanium tetrachloride for titanium oxychloride concentration because vanadium passivated titanium tetrachloride streams can contain tenacious solids, as high as 50 to 60%, which are difficult to deal with in the analytical equipment which is needed to detect the presence (or absence) of substances such as titanium oxychloride. Consequently, it is important that neither the Cronin publication nor any other references of record

disclose detecting the absence of titanium oxychloride in the vanadium passivated titanium tetrachloride in order to make a determination about mixing an aluminum passivating agent into the vanadium passivated discharge as recited in the present claims.

Claim 14

Claim 14 should be separately considered by the Board.

Claim 14 is directed to mixing the vanadium passivating agent into the chlorinator discharge in an amount sufficient to reduce the concentration of, but not eliminate, the vanadium chlorides.

Nothing in the cited references has been pointed to which teaches or suggests the obviousness of mixing the vanadium passivating agent into the chlorinator discharge in an amount sufficient to reduce the concentration of, but not eliminate, the vanadium chlorides. A two step addition of the vanadium passivating agent does not eliminate the vanadium chlorides in the chlorinator discharge. The two step process improves raw material utilization by minimizing the amount of passivating agent. When titanium oxychloride is not present, an amount of aluminum passivating agent sufficient to form titanium oxychloride is added to form easy-to-separate aluminum-containing compounds, see the specification at page 4, line 36 to page 5, line 2. The rejection of claim 14 is in error because nothing in the cited references has been pointed to which teaches or suggests that it would have been prima facie obvious to mix the vanadium passivating agent into the chlorinator discharge in an amount sufficient to reduce the concentration of, but not eliminate, the vanadium chlorides in a process for purifying a crude titanium tetrachloride chlorinator discharge as recited in the instant claim.

Claim 19

Claim 19 should be separately considered by the Board.

Claim 19 depends from claim 14 and further comprises after the separating step, mixing the vanadium passivating agent into the passivated discharge in a second amount to eliminate the vanadium chlorides.

Nothing in the cited references has been pointed to which teaches or suggests that it would have been prima facie obvious to mix the vanadium passivating agent into the chlorinator discharge in an amount sufficient to reduce the concentration of, but not eliminate, the vanadium chlorides, when titanium oxychloride is not present, mixing aluminum passivating agent sufficient to form titanium oxychloride and mixing the vanadium passivating agent into the passivated discharge in a second amount sufficient to eliminate the vanadium chlorides.

The rejection of claim 19 is in error because nothing in the cited references has been pointed to which teaches or suggests the prima facie obviousness of the two step process as recited in the instant claim 19.

**Rejection under 35 U.S.C. §103(a) in view of U.S. Patent No. 2,600,881 of Kay et al. ("the '881 patent") in view of U.S. Patent No. 2,592,021 of Frey et al. ("the '021 patent") and the Cronin et al. publication**

Claims 12-13 and 15-18

Claims 12-13 and 15-18 are considered to stand or fall together.

In rejecting claims 12-13 and 15-18, the Examiner relied on the '881 patent for teaching removal of aluminum chloride in solution with liquid titanium tetrachloride which comprises mixing an amount of water sufficient only to react with the active aluminum chloride to be removed. The '881 patent was additionally relied on for teaching the undesirability of excess water to avoid loss of titanium values. The '881 is further relied on for suggesting the removal of vanadium at Col. 6, lines 30-35 after removal of aluminum chloride. Reliance is then placed on the '021 patent for disclosing the removal of coloring impurities from titanium tetrachloride by mixing the titanium tetrachloride containing vanadium chloride impurities with an organic compound such as a hydrocarbon oil such as "petrol, crude oil, benzene, liquid paraffin, cracking gases, animal and vegetable



fats and oils, etc.” see Col. 3, lines 21-23. From this combination of references, the view is taken that one of ordinary skill in the art would have found it obvious to remove the vanadium impurity from the titanium tetrachloride of the '881 patent because the '021 patent provides “an easy and cheap way of removing impurity from titanium tetrachloride”.

The Cronin et al. publication is then relied on for teaching an in process, real-time control loop for monitoring the presence of titanium oxychloride in order to decide the addition of the aluminum passivating agent.

Ex parte Rubin, 128 USPQ 440 (Bd. App. 1959) and In re Burhans 154 F.2d 690, 69 USPQ 330 (CCPA 1946) are relied on for concluding that the order of performing process steps by removing vanadium before the step of removing aluminum as recited in the instant claims would have been prima facie obvious in the absence of new or unexpected results. These cases stand for the proposition that an obviousness conclusion can be reached in the absence of any proof that the order of performing steps produces an unexpected result. However, the finding that the order of process steps is the key difference between the claims and the disclosure of the cited references overlooks important features recited in the claims. In ex parte Rubin, the Patent Office Board of Appeals considered a situation where the claims were directed to a method of forming a laminated sheet in which only the order of steps was changed and according to the record, the same product was obtained and the method of the prior art was considered to be better than the claimed method. In contrast, the '881 patent which discloses inactivating aluminum chloride in titanium tetrachloride and after distillation freeing the titanium tetrachloride from color-imparting impurities such as a chloride of vanadium by an additional treatment such as by distillation over a copper contact mass would not have suggested or made obvious the claimed step of detecting titanium oxychloride in the vanadium passivated discharge and if absent mixing an aluminum passivating agent into the passivated discharge in an amount sufficient to passivate the aluminum chloride and react with the titanium tetrachloride to form titanium oxychloride because there is no recognition in the '881 patent, or any other reference of record, that detecting titanium oxychloride indicates aluminum chloride passivation. In the absence of the discovery that a passivating agent for aluminum

chloride forms from passivation of vanadium chloride, it would not have been obvious to the person of ordinary skill in the art of crude titanium tetrachloride passivation to detect titanium oxychloride in the vanadium passivated discharge in order to recognize that only if titanium oxychloride is absent is an aluminum chloride passivating agent required. Moreover, a person of ordinary skill in the art of crude titanium tetrachloride passivation would not have even considered trying to analyze the vanadium passivated titanium tetrachloride because vanadium passivated titanium tetrachloride streams can contain tenacious solids, as high as 50 to 60%, which are difficult to deal with in the analytical equipment which is needed to detect the presence (or absence) of substances such as titanium oxychloride. As such, the finding that the claims have a different order of removing aluminum and vanadium which would have been obvious because any order of performing process steps is prima facie obvious in the absence of new or unexpected results is in error. Accordingly, a proper prima facie showing of obviousness has not been made.

Claim 14

Claim 14 should be separately considered by the Board.

Claim 14 is directed to mixing the vanadium passivating agent into the chlorinator discharge in an amount sufficient to reduce the concentration of, but not eliminate, the vanadium chlorides.

Nothing in the cited references has been pointed to which teaches or suggests the obviousness of mixing the vanadium passivating agent into the chlorinator discharge in an amount sufficient to reduce the concentration of, but not eliminate, the vanadium chlorides. A two step addition of the vanadium passivating agent does not eliminate the vanadium chlorides in the chlorinator discharge. The two step process improves raw material utilization by minimizing the amount of passivating agent. When titanium oxychloride is not present, an amount of aluminum passivating agent sufficient to form titanium oxychloride is added to form easy-to-separate aluminum-containing compounds, see the specification at page 4, line 36 to page 5, line 2. The rejection of claim 14 is in error because nothing in the cited references has been pointed to which teaches or suggests that it would have been prima facie obvious to mix the vanadium passivating agent into the chlorinator discharge in an amount sufficient to reduce the concentration of, but not eliminate, the vanadium

chlorides in a process for purifying a crude titanium tetrachloride chlorinator discharge as recited in the instant claim.

Claim 19

Claim 19 should be separately considered by the Board.

Claim 19 depends from claim 14 and further comprises after the separating step, mixing the vanadium passivating agent into the passivated discharge in a second amount to eliminate the vanadium chlorides.

Nothing in the cited references has been pointed to which teaches or suggests that it would have been prima facie obvious to mix the vanadium passivating agent into the chlorinator discharge in an amount sufficient to reduce the concentration of, but not eliminate, the vanadium chlorides, when titanium oxychloride is not present, mixing aluminum passivating agent sufficient to form titanium oxychloride and mixing the vanadium passivating agent into the passivated discharge in a second amount sufficient to eliminate the vanadium chlorides.

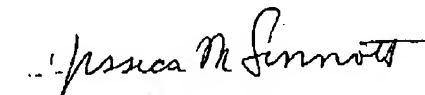
The rejection of claim 19 is in error because nothing in the cited references has been pointed to which teaches or suggests the prima facie obviousness of the two step process as recited in the instant claim 19.

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**CONCLUSION**

For the reasons set forth it is submitted that the Examiner's rejections are improper and should be reversed, which action is earnestly solicited.



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Date: April 1, 2008

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**(viii) CLAIMS APPENDIX**

12. In an improved process for purifying a crude titanium tetrachloride chlorinator discharge from the carbochlorination of titanium-containing materials comprising titanium tetrachloride, aluminum chloride and vanadium chlorides, by mixing a vanadium passivating agent selected from the group consisting of organic oil into the chlorinator discharge to form a passivated discharge comprising one or more easy-to-separate vanadium-containing compounds, wherein the improvement comprises:

(a) detecting, in the passivated discharge, titanium oxychloride formed therein, and, if titanium oxychloride is absent, mixing an aluminum passivating agent into the passivated discharge in an amount sufficient to passivate the aluminum chloride and react with the titanium tetrachloride to form titanium oxychloride, the aluminum passivating agent being selected from the group consisting of water, water containing solutions, water containing mixtures, and carboxylic acid to form one or more easy-to-separate aluminum-containing compounds in the passivated discharge; and

(c) separating from the passivated discharge the easy-to-separate vanadium- and aluminum-containing compounds to form a purified titanium tetrachloride.

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13. The process of Claim 12 wherein the separation process is selected from the group consisting of flashing distillation, multi-stage distillation, a solid-liquid separation process, filtration, and centrifugation.
14. The process of Claim 12 wherein the vanadium passivating agent is mixed into the chlorinator discharge in an amount sufficient to reduce the concentration of, but not eliminate, the vanadium chlorides.
15. The process of Claim 12 wherein the aluminum passivating agent is comprised of a purge-containing product from the passivation of vanadium chlorides taken from a process step following the separation step.
16. The process of Claim 12 wherein the mixing of the vanadium passivating agent and the aluminum passivating agent are controlled by a process control method.
17. The process of Claim 12 wherein the vanadium passivating agent is a petroleum oil, an animal fat, a vegetable oil or a combination thereof
18. The process of Claim 12 wherein the vanadium passivating agent is a hydrogenated naphthenic oil.
19. The process of Claim 14 further comprising after step (c) mixing the vanadium passivating agent into the passivated discharge in a second amount sufficient to eliminate the vanadium chlorides.

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**(ix) EVIDENCE APPENDIX**

- (a) U.S. Patent No. 4,246,022 of Robinson (see March 24, 2006 Office action)
- (b) Great Britain Patent No. 744,074 (see December 31, 2007 final Office action)
- (c) Australian Patent No. 219,385 (see March 24, 2006 Office action form PTO/SB/08A)
- (d) U.S. Published Patent Application No. 2001/0016182 of Cronin et al. (see December 31, 2007 final Action)
- (e) U.S. Patent No. 2,600,881 of Kay et al. (see December 31, 2007 final Action)
- (f) U.S. Patent No. 2,592,021 of Frey et al. (see December 31, 2007 final Action)
- (g) Ex parte Rubin 128 USPQ 440 (Pat. Office Bd. of App. 1959) (see December 31, 2007 final Action)
- (h) In re Burhans 69 USPQ 330 (CCPA 1946) (see December 31, 2007 final Action)

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**(x) RELATED PROCEEDINGS APPENDIX**

NONE



**United States Patent** [19]**Robinson**[11] **4,246,022**[45] **Jan. 20, 1981**[54] **PROCESSING METAL CHLORIDES**[75] **Inventor:** Michael Robinson, Wooton, England[73] **Assignee:** Laporte Industries Limited, London, England[21] **Appl. No.:** 30,112[22] **Filed:** Apr. 16, 1979[30] **Foreign Application Priority Data**

May 5, 1978, [GB] United Kingdom ..... 17932/78

[51] **Int. Cl.** ..... C22B 55/00[52] **U.S. Cl.** ..... 75/11; 75/1 T;

75/10 R; 75/84

[58] **Field of Search** ..... 75/21, 1 T, 29, 84,  
75/10 R, 11, 84.5[56] **References Cited****U.S. PATENT DOCUMENTS**3,859,077 1/1975 Other ..... 75/1 T  
3,989,510 11/1976 Other ..... 75/21**Primary Examiner**—M. J. Andrews**Attorney, Agent, or Firm**—Kane, Dalsimer, Kane, Sullivan and Kurucz[57] **ABSTRACT**

Metal may be recovered from metal chlorides, for example a mixed metal chloride residue from the fluidized bed chlorination of a titaniferous ore in the presence of carbon to produce titanium tetrachloride by heating, in the presence of a scavenging agent, which may comprise a combination of titanium dioxide and carbon inherently present in a residue from the aforesaid fluidized bed chlorination process, to at least 1500° C. and preferably to a temperature at which iron present is liquid. If the temperature is maintained at below 2200° C. iron, vanadium and niobium may be recovered preferentially to certain lower value metals which remain in the form of chlorides giving the possibility for the recovery of a high value mixed metal product. Titanium trichloride may be formed and this may be chlorinated to titanium tetrachloride thereby increasing the efficiency of the original chlorination process.

**9 Claims, No Drawings**

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## PROCESSING METAL CHLORIDES

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

This invention relates to the processing of metal chlorides and the recovery, therefrom, of metal.

## 2. Brief Description of the Prior Art

Titanium tetrachloride may be produced by chlorinating a titaniferous material which, typically, contains at least 90% by weight of titanium dioxide either because it comprises a titanium-rich ore such as rutile or because it comprises an ore beneficiate or synthetic rutile from which a large proportion of the iron originally in the ore has been removed. The chlorination is followed by the purification of the titanium tetrachloride vapour produced and the accumulation in the course of such purification of one or more residues which, typically, contain iron compounds but which may also contain chlorides of high value metals, such as niobium or vanadium and chlorides of relatively low value metals such as aluminium, magnesium, calcium and manganese.

Particularly, in the chlorination of a titaniferous ore such as rutile or synthetic rutile ore, in a fluidised bed in the presence of carbon the stream of gases issuing from the fluidised bed contains

1. Blow-over dust, e.g.  $\text{TiO}_2$ , C,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZrSiO}_4$ .
2. Vaporous chlorides of the minor constituents of the ore.
3. Residual inert gas and carbon oxides.
4. Titanium tetrachloride vapour.

This effluent stream may be cooled to condense some of the chlorides, notably iron chlorides and niobium chloride, without condensing any substantial quantity of titanium tetrachloride and passed to a cold cyclone where such condensed materials and blow-over dust are substantially removed from the stream. The titanium tetrachloride may then be condensed to separate it from residual inert gases and carbon oxides and purified by treatment with mineral oil, a mineral oil sludge residue often containing aluminium chloride, niobium chloride and vanadium chloride thereby being produced.

It would be desirable to recover the high value metals from metal chloride residues. Particularly, the cyclone and oil purification residues from titanium tetrachloride production, combined or separately, provide a relatively concentrated source of high value metals, e.g. niobium and/or vanadium, if they can be recovered effectively and economically from the chloride form in which they are present in the residues and, preferably, fractionated to some extent from the low value metals also present. A typical combined cyclone and oil purification residue from a titaniferous ore chlorination process for the production of titanium tetrachloride can contain, for each mole of titanium tetrachloride produced, up to about 0.0075 moles of vanadium chloride and up to about 0.005 moles of niobium chloride and, assuming the producing unit to be on a commercial scale, the equivalent annual quantities of vanadium metal and niobium metal present in the residue amount of hundreds of tons.

British Pat. No. 1,250,913 relates to a process for treating a vanadium, zirconium or chromium-containing residue from the chlorination of titaniferous ore, to facilitate the recovery of vanadium therefrom, comprising treating the residue with water in an amount insufficient to slurry the residue but at least sufficient theoretic-

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cally to react with all the chlorine of the residue and heating the so-treated residue in a free oxygen-containing atmosphere at a temperature of at least 300° C. to remove the major part of the chlorine as hydrogen chloride to ease the recovery of vanadium, zirconium or chromium as oxides. The said recovery is a chemical process involving treatment with an alkali or acid to provide solutions which, by conventional techniques, give rise to the separate constituent metals.

The U.S. Bureau of Mines Report R1 7671 (1972) describes a process for the separation of columbium (niobium), tantalum, titanium, and zirconium from mineral waste from the chlorination of rutile ore. The process described is a liquid-liquid extraction process involving the use of a 10-stage reactor.

## SUMMARY OF THE INVENTION

The present invention relates to a process for the direct recovery of metals from metal chlorides. The invention is particularly applicable to the treatment of residues from the production of titanium tetrachloride by the chlorination of a titaniferous material. The invention is also applicable to other metal chloride residues, from whatever source, subject to the presence of a sufficiently high proportion of compounds of high value metals to render the use of the invention economic.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

The present invention provides a process for the treatment of metal chloride to recover metal therefrom characterised by establishing a mixture of metal chloride and a chlorine scavenger, causing the metal chloride to react with the chlorine scavenger by heating them to a temperature of at least 1500° C. and separating the resulting metal from the resulting chlorine-loaded scavenger.

One class of chlorine scavenger which is suitable for use in the practice of this invention comprises a combination of a metal oxide capable of forming metal chlorides volatile at the temperature involved and a de-oxidant.

Preferably the metal oxide is titanium dioxide, although alumina or silicon dioxide may, alternatively, be usable. Preferably the metal oxide has a particle size no greater than 500 and, particularly preferably, no greater than 175 microns. Preferably the de-oxidant is a form of carbon, for example, coke. Preferably the de-oxidant has a particle size of no greater than 3500 microns and particularly preferably, no greater than 500 microns. In use, the metal oxide forms volatile metal chloride, for example titanium chloride, the de-oxidant may combine with the oxygen released to form carbon oxides and the metal of the original metal chloride may remain in the metallic state for recovery. The metal oxide and the carbon are preferably used in at least the theoretical quantity to fulfil their purpose, that is, to react with the quantity of metal chloride reactive at the temperature employed which is present and, particularly preferably, are used in an excess over that quantity, for example, an excess of from 50% to 250%.

It is a particularly advantageous feature of this invention that metal chloride residues recovered from effluent gases from the fluidised bed chlorination of a titaniferous ore carried out in the presence of carbon may be

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treated directly, by applying the required temperature thereto, since they inherently contain a chlorine scavenger by reason of their content of titanium dioxide and of carbon in the form of blow-over dust for the operation of the invention. Generally the chlorine scavenger is present in a suitable quantity.

Preferably the mixture of metal chloride and chlorine scavenger is heated to a temperature such that at least the iron component of the product metals is in the liquid form. Since the iron component is a product component this may enable the product mixed metals, even if some are at temperatures below their individual melting points, to be tapped or poured from the product receiving vessel and, if desired, directly cast into ingots. Certain metals, notably iron, tend to volatilise at about 3000° C. and the mixture of metal chloride and chlorine scavenger is therefore heated to as a preference below such temperature.

We have found that a certain degree of separation of more valuable from less valuable metals is possible by further particular control of the temperature within the broad indication given above. If the mixture of metal chloride and chlorine scavenger is heated to below about 2200° C. at least a proportion of chlorides of the less valuable metals, for example some or more of aluminium, zirconium, manganese, magnesium and calcium, fails to react with the chlorine scavenger with the effect that said proportion, which is volatilised, may be led off as vapour. To attain efficient operation of the invention the mixture of metal chloride and chlorine scavenger is preferably heated to at least 1700° C. at which temperature the metals product is more readily recovered than at lower temperatures.

The metal product of this invention may mainly comprise a mixture of iron together with vanadium and/or niobium. Where an ore containing little iron has been chlorinated to produce titanium tetrachloride, for example rutile ore, the metal product obtained by the practice of this invention may comprise not more than 50% for example from 20% to 50%, by weight of iron. The metal product of the invention may contain up to about 25% for example from 10% to 25% by weight of vanadium and/or niobium.

Where the invention is operated using a chlorine scavenger including titanium dioxide the titanium chloride produced mainly comprises titanium trichloride although at higher temperatures titanium dichloride may be formed. Titanium trichloride is a desirable by-product since it is readily recovered from inert gases and carbon oxides by condensation. It may be readily chlorinated to titanium tetrachloride. The quantity of extra titanium tetrachloride which may be generated in this manner may be over 0.05 moles per mole of titanium tetrachloride produced by ore chlorination and therefore represents an appreciable increase in the efficiency of the titanium tetrachloride production process from which the residues treated by the invention were derived.

The further chlorination of the lower chloride is exothermic and is readily accomplished merely by contact, in the vapour phase with chlorine gas. Preferably the chlorination is conducted by directly contacting the gaseous stream containing the lower chlorides with chlorine. Preferably the further chlorination is conducted at a temperature of at least 1000° C. but below 2200° and, particularly preferably below 1500° C.

The present invention may be carried out in any of a variety of electrical discharge furnaces capable of im-

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parting temperatures in excess of 1500° C. to a particulate solid feed. Alternatively, the process may be conducted in an electrical induction furnace which has the advantage of not being subject to interference with a discharge by particles being treated, or products of that treatment, for example iron in liquid form, some of which may be electrically conductive. Suitably the process is conducted by allowing a mixture of metal chloride and chlorine scavenger to fall through a reaction chamber capable of imparting the requisite temperature to the falling stream.

The practice of the present invention may give rise to the formation of phosgene. Normal precautions applicable to gases containing phosgene should therefore be applied.

An Example of the practice of this invention will now be described.

#### EXAMPLE

Titanium tetrachloride was produced by the chlorination of particles of rutile ore in admixture with particles of carbon in a fluidised bed. The hot titanium tetrachloride-containing gas stream issuing from the bed was passed into a cyclone maintained at 200° C. which acted to condense certain metal chlorides from the gas stream and to recover these together with carbon dust to form a residue. The titanium tetrachloride was condensed separately and purified by treating it with an oil to produce a further residue. The residues thereby obtained were mixed and the mixed residue contained.

23% titanium oxide  
44% carbon  
1.1% silicon oxide  
4.5% zirconium oxide  
8.2% iron chloride  
2.5% chromium chloride  
5.9% vanadium chloride  
5.5% aluminium chloride  
5.3% niobium chloride

A charge of 125 g of the mixed residue was placed in the crucible of a Raydyno 10 kilowatt induction heater model C95. The crucible was of graphite, was cylindrical, with one closed end and the dimensions length 18 cm, external diameter 8 cm and internal diameter 3 cm, and was positioned horizontally supported on an axial rotatable graphite rod protruding from the closed end. At the other end to the rod the crucible was fitted with a graphite screw plug to seal in the charge and to prevent the volatile metal chlorides venting to the atmosphere. A 7 mm diameter hole was drilled in the body of the crucible to come within 2 mm of the inner surface and to accommodate a withdrawable iridium/iridium 40% rhodium thermocouple. The crucible was surrounded by the induction coil with a space therebetween thermally insulated with ceramic wool, and the coil/crucible assembly was contained in an asbestos box.

The crucible, containing the charge, was rotated at 25 rpm and electrical power was applied to the coil. Periodically, the power was switched off, the rotation stopped and a temperature measurement made with the withdrawable thermocouple. A temperature of 1700° C. was achieved and maintained for 30 minutes. Power was switched off and the system allowed to cool.

When the crucible was cool the screw plug was removed and there was a release of pressure. There were a few crystals of a purple compound, which on analysis was shown to be  $TiCl_3$ , and a slag like material

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was also found. When the slag was broken up some beads of metal were found which weighed 3.0 grams. This metal was analysed by X-ray fluorescence and found to have almost equal atomicities of vanadium and niobium with double the atomicity of iron.

I claim:

1. A process for treating a mixture of metal chlorides comprising iron chloride and a compound selected from the group consisting of vanadium chloride, niobium chloride and mixtures thereof to recover the corresponding metals therefrom, which comprises;

establishing a mixture of the metal chlorides and a chlorine scavenger which comprises a combination of carbon and a metal oxide capable of forming a corresponding volatile metal chloride at the temperature to which the mixture of metal chlorides and the chlorine scavenger are heated as hereinafter described;

causing the metal chlorides to react with the chlorine scavenger by heating their mixture to a temperature of at least 1,500° C.; and

separating said corresponding metals from the resulting chlorine-loaded scavenger.

2. A process as claimed in claim 1 conducted in an electrical discharge furnace.

3. A process as claimed in claim 1 conducted in an electrical induction furnace.

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4. A process as claimed in claim 1 wherein the metal oxide is selected from titanium dioxide, silicon dioxide and alumina;

5. A process as claimed in claim 1 wherein the carbon is in the form of particles having a size no greater than 3500 microns and the metal oxide is in the form of particles having a size no greater than 500 microns.

6. A process as claimed in claim 1 wherein the carbon and the metal oxide are present in an excess over the quantity required in theory having regard to the quantity of metal chloride reactive with the chlorine scavenger at the temperature employed.

7. A process as claimed in claim 1 wherein metal chloride to be treated comprises a residue recovered from effluent gases from the fluidised bed chlorination of an iron-containing titaniferous ore carried out in the presence of carbon, the residue containing a chlorine scavenger by reason of its content of titanium dioxide and of carbon.

8. A process as claimed in claim 1 wherein the metal chloride to be treated and the chlorine scavenger are heated to a temperature such that iron present would be in the liquid form.

9. A process as claimed in claim 1 wherein the metal chlorides to be treated further comprises, at least one chloride of aluminium, zirconium, manganese, magnesium and calcium the metal chloride to be treated and the scavenger being heated to a temperature below 2200° C.

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UNITED STATES PATENT AND TRADEMARK OFFICE  
CERTIFICATE OF CORRECTION

PATENT NO. : 4,246,022  
DATED : January 20, 1981  
INVENTOR(S) : Michael Robinson

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 4, line 42; "grapite" should read -- graphite -- .

Column 6, Claim 9; Delete Claim 9 in its entirety.

**Signed and Sealed this**

*Fourteenth Day of April 1981*

[SEAL]

*Attest:*

RENE D. TEGMEYER

*Attesting Officer*

*Acting Commissioner of Patents and Trademarks*

# RESEARCH

## PATENT SPECIFICATION 744,074



*Date of Application and filing Complete Specification: June 8, 1953.*

*No. 15770/53.*

*Application made in United States of America on June 12, 1952.*

*Complete Specification Published: Feb. 1, 1956.*

Index at Acceptance:—Class 1(3) A1D(10:30), A1G34D1O, A1G37D(10:30).

### COMPLETE SPECIFICATION

#### Improvements in or relating to the purification of titanium tetrachloride

We, NATIONAL LEAD COMPANY, a Corporation organised and existing under the Laws of the State of New Jersey, United States of America, of 111, Broadway, New York 6, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is for improvements in or relating to the purification of titanium tetrachloride.

15 In general the tetrahalides of metals of the fourth group of elements are prepared by chlorinating a metal bearing material and recovering the metal tetrachloride vapour in the form of a relatively impure liquid condensate. By way of example, liquid titanium tetrachloride is commonly prepared by treating a titaniferous material such as titaniferous iron ore, or ilmenite with chlorine gas, in a static bed or fluo-solids operation, 25 to form titanium tetrachloride vapour which is subsequently condensed to form a crude titanium tetrachloride condensate. Since there are a number of elements in the raw material, in addition to titanium, which react with chlorine to form volatile chlorides and which carry over with the titanium tetrachloride vapours, the titanium tetrachloride condensate, sometimes hereinafter referred to as crude titanium tetrachloride, 35 is invariably impure. Moreover, it has been found that these volatile chlorides are not readily eliminated by distillation since the respective chlorides such as, for example, the chlorides of silicon, aluminium, niobium, tungsten and vanadium, tend to distil over with the titanium tetrachloride values and to be found in the condensate. One such impurity which, because of the proximity of

its boiling point to that of titanium tetrachloride, cannot be separated therefrom by 45 fractional distillation, is vanadium chloride. Vanadium chloride is present in substantially all crude titanium tetrachloride condensate and comprises a major portion of the impurities in the condensate and 50 hence is chiefly responsible for the yellowish colour of crude titanium tetrachloride. By way of example, a typical crude titanium tetrachloride may comprise from 0.25 to 0.35% vanadium based on the weight of 55 the titanium tetrachloride the other impurities being present in relatively small amounts such as, for example, from 0.04 to 0.2% silica, from 0.02 to 0.025% alumina, from 0.01 to 0.02% niobium and from 0.05 to 60 0.08% tungsten.

While it has been proposed heretofore to purify crude titanium tetrachloride and other similar tetrahalides by treatment with such materials as hydrogen sulphide, silica gel, 65 carbon, salts of the heavy metals, soya bean oil and art gum, such methods have been characterized by the formation of residues which have been either insoluble or removable from the still bottoms only with the 70 greatest difficulty. As a consequence the adaptation to commercial production of prior methods for purifying crude titanium tetrachloride have been attended by much difficulty and high cost. 75

An object of the invention is, therefore, to provide a superior method for purifying crude titanium tetrachloride which is convenient, economical and adapted to commercial production. 80

A still further object of the invention is to provide a superior method for removing a major portion of the impurities from crude titanium tetrachloride in a manner such that no polymerization occurs and the residue 85 formed may be readily removed from the still.

[Price 3s. 0d.]

Price 3s. 6d.

Price 4s. 6d.  
Price 2s. 6d.

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According to the present invention there is provided a process for purifying crude titanium tetrachloride to remove a major portion of the impurities therefrom which comprises refluxing the crude titanium tetrachloride in the presence of animal waxes in the proportion of not more than 0.2% based on the weight of the crude titanium tetrachloride.

- 10 As used herein the term animal wax sometimes hereinafter referred to as a purifying agent, has reference to a specific group of waxes identified in the Table of Constants of Fats, Oils and Waxes on page 15 678 of Lang's Handbook of Chemistry, 5th Edition, published by the Handbook Publishers, Inc., namely:

Wool-fat (wax).

Spermaceti.

- 20 Beeswax.

The animal waxes have been found to serve as a highly satisfactory purifying agent for crude titanium tetrachloride; and to form a non-polymerized residue.

- 25 The treatment of crude titanium tetrachloride, by which is meant a liquid titanium tetrachloride containing impurities such for example as vanadium, silica, alumina, niobium and tungsten, with the animal wax may be carried out, in any convenient manner which will ensure the required intimacy of contact between the crude titanium tetrachloride and the purifying agent. Preferably the purification treatment is carried 35 out in a purification unit comprising, for example, a still having a fractionating column, a reflux return and a condenser, by heating the crude titanium tetrachloride with an animal wax in the still to a temperature 40 and for a period of time such that substantially all of the titanium tetrachloride is circulating as vapour through the fractionating column and reflux return, and thereafter allowing the vapour to pass to the condenser 45 in which the titanium tetrachloride will be condensed and collected as a water-white liquid. The heating of the liquids and recirculation of the vapour is sometimes hereinafter referred to as refluxing.

- 50 The residue which forms in the bottom of the still is generally a relatively hard granular substance which may be readily removed from the still and which, before being washed, has been identified by X-ray 55 patterns as comprising a mixture of rutile, anatase, free carbon and impurities the principle one of which is vanadium.

- The aforesaid relatively hard granular residue comprises titanium dioxide, vanadium, and small amounts of silica, alumina, 60 tungsten, niobium and other impurities the vanadium being in the form of  $VOCl_3$  and/or  $VOCl_2$ , which may be recovered from the residue by water leaching. It has been ob- 65 served that the vanadium content of crude

liquid titanium tetrachloride may be reduced by the process of this invention from about 0.35% by weight of titanium tetrachloride as found in crude titanium tetrachloride to about 0.0001%, the purified liquid titanium 70 tetrachloride being water-white.

The term "water-white" is used herein to denote a substantially pure titanium tetrachloride condensate. In particular a titanium tetrachloride condensate purified by the 75 process of this invention and defined as water-white is one having a major portion of its impurities removed i.e. the maximum vanadium content is in the range of from about 0.0001% to 0.0003% by weight of the 80 titanium tetrachloride, the remaining impurities in the titanium tetrachloride condensate being present in such small quantities as to be innocuous.

The time and temperature of treatment is 85 dependent to some extent upon the amount of impurities in the crude titanium tetrachloride and upon the amount of the purifying agent used to remove the impurities from the titanium tetrachloride. Moreover, the 90 amount of the purifying agent used is, in turn, dependent upon the amount of impurities and in particular the amount of vanadium present in the crude titanium tetrachloride.

In carrying out the treatment of the crude 95 titanium tetrachloride, the animal wax is usually added to crude titanium tetrachloride at substantially room temperature whereupon the mixture is heated to a temperature of from 134°C to 138°C for a period of time, 100 generally in the neighbourhood of about 2 hours, after which the titanium tetrachloride vapours are condensed to form substantially water-white titanium tetrachloride. The length of time necessary for effective treat- 105 ment of the crude liquid titanium tetrachloride varies inversely with the amount of animal wax added to the crude titanium tetrachloride. For economical reasons a minimum amount of animal wax for effecting substantially complete purification of the 110 crude titanium tetrachloride is preferred and where a minimum amount of animal wax is added such as, for example, substantially 0.1% based on the weight of the crude 115 titanium tetrachloride the time required for refluxing the mixture of crude titanium tetrachloride and the animal wax is about 2 hours. However, it has been observed that when the amount 120 of animal waxes is substantially 0.2% then the reflux time is about 1 hour. In short as the amount of purifying compound added to the crude titanium tetrachloride is increased the time required for refluxing the admixture 125 of crude titanium tetrachloride and the purifying compound is decreased.

Following is a description by way of example of methods of carrying the inven- 130 tion into effect.

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## EXAMPLE

0.1 part of wool fat was added to 100 parts of crude titanium tetrachloride at substantially room temperature, refluxed at a temperature of about 136°C for a period of 2 hours, and distilled to yield a clear water-white titanium tetrachloride.

By the process of this invention crude titanium tetrachloride comprising impurities the major portion of which is vanadium may be purified by refluxing the titanium tetrachloride in the presence of an animal wax wherein a relatively small quantity of the animal wax is required and a substantially pure water-white titanium tetrachloride condensate is produced in an economical, convenient and commercially practical manner.

What we claim is:

1. A process for purifying crude titanium tetrachloride to remove a major portion of the impurities therefrom which comprises refluxing the crude titanium tetrachloride in the presence of animal waxes in the proportion of no more than 0.2% based on the weight of the crude titanium tetrachloride.

2. A process as claimed in claim 1 wherein the impurities comprise vanadium, a mixture is formed of the crude titanium tetra-

chloride and the animal waxes and the mixture is refluxed at a temperature and for a period of time sufficient to produce a water-white titanium tetrachloride condensate.

3. A process as claimed in either of the preceding claims wherein the animal wax is spermaceti.

4. A process as claimed in claim 1 or claim 2 wherein the animal wax is beeswax.

5. A process as claimed in claim 1 or claim 2 wherein the animal wax is wool fat.

6. A process as claimed in any one of the preceding claims wherein the proportion of animal waxes is substantially 0.1% based on the weight of crude titanium tetrachloride.

7. A process as claimed in any one of the preceding claims wherein the mixture is refluxed at a temperature of approximately 136°C. for a period of approximately 50 2 hours.

8. A process for purifying crude titanium tetrachloride substantially as described with reference to the specific example hereinbefore set forth.

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to public inspection quoting  
claim no. .... was received  
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## COMMONWEALTH OF AUSTRALIA

## PATENT SPECIFICATION

Complete Specification lodged .. .. 24th September, 1957.  
Application lodged No. 31,545/57 .. .. 24th September, 1957.  
Applicant .. .. Laporte Titanium Limited.  
Actual Inventor .. .. Raymond James Wigginton.

Convention Application.  
(Great Britain, 25th September, 1956.)

Complete Specification Published .. .. 27th March, 1958.  
Complete Specification Accepted .. .. 8th December, 1958.

Classification: 08.4.

No drawing.

## COMPLETE SPECIFICATION.

## " Process for the purification of titanium tetrachloride."

The following statement is a full description of this invention, including the best method of forming it known to us:

It is known to purify liquid titanium tetrachloride containing vanadium as an impurity by heating the tetrachloride with a small proportion of an organic material (see, for example, United States Specifications Nos. 10,538 and 2,592,021 and British Specification No. 656,098). The organic materials are those which are capable of undergoing carbonisation, probably preceded by merisation, in the presence of the titanium tetrachloride under the conditions used, for example, when the impure titanium tetrachloride and the organic material are heated above the boiling point of titanium tetrachloride. The vanadium impurity and, when present, certain other metallic impurities, for example, iron and chromium, are taken up in the solid products of carbonisation, and removed by separating the solid carbonisation products from the liquid titanium tetrachloride, for example, by distilling off the tetrachloride or by filtration or centrifuging.

Organic materials that carbonise slowly, for example, saturated aliphatic hydrocarbons, such as liquid paraffin, are satisfactory as purifying agents only at temperatures above the boiling point of titanium tetrachloride or if a mixture of liquid titanium tetrachloride and the organic material is boiled under reflux for several hours. More readily carbonisable materials, such as vegetable oils or mineral oils containing unsaturated hydrocarbons, have a greater purifying power, but they tend to contaminate the purified product with organic substances which subsequently impart a dark colour to the product when it is distilled. Such contamination is undesirable for some purposes for which the titanium tetrachloride is to be used, for example, for the manufacture of titanium metal.

The present invention provides a process for the purification of titanium tetrachloride containing vanadium as an impurity, wherein the impure liquid titanium tetrachloride is heated with a small proportion of a carbonisable organic material in the presence of a proportion of finely divided metallic sodium

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amounting to about 5 to 50 per cent. calculated on the weight of the organic material to bring about carbonisation of the organic material, and the purified titanium tetrachloride is separated from the solid carbonisation products containing the impurities.

The presence of the finely divided metallic sodium has the effect of accelerating the purifying action of the organic material, and therefore enables the throughput of titanium tetrachloride to be purified to be increased and/or the proportion of the organic material, and consequently the amount of waste residue for disposal, to be decreased. Moreover, the extent to which the purified titanium tetrachloride is contaminated with organic matter can be reduced by using organic materials that carbonise slowly and without the long reaction periods that such materials normally require. Furthermore, the quantity of certain other impurities in the final product, such as free chlorine and hydrogen chloride, is less since the sodium reacts with them.

The temperature at which the titanium tetrachloride is heated with the organic material and the metallic sodium is preferably at least 100° C. The heating may be carried out under atmospheric pressure or a higher or lower pressure. Advantageously, the titanium tetrachloride is heated in the liquid state with the organic material and the metallic sodium under atmospheric pressure at a temperature within the range of 100° C. up to the boiling temperature of titanium tetrachloride, viz 136° C. A convenient method is to boil the titanium tetrachloride under reflux in the presence of the organic material and metallic sodium. Any organic material capable of undergoing carbonisation when heated in liquid titanium tetrachloride may be used, for example, the materials used in the known processes referred to above. The proportion of the organic material is advantageously within the range of 0.1 to 1.0 per cent. calculated on the weight of the titanium tetrachloride to be purified. The organic material is advantageously one which, when used alone, is slowly carbonisable, since such materials are generally less costly than the more reactive materials and so greater benefit is derived from the accelerating action of the finely divided metallic sodium. As slowly carbonisable materials there are meant carbonisable saturated or unsaturated organic

materials having an iodine value not exceeding 25. Such organic materials are mineral oils, such as crude petroleum oil or petroleum distillates, which are saturated or have a content of unsaturated compounds such that their iodine value does not exceed 25. Alternatively, there may be used vegetable or animal oils, fats or waxes, which do not exceed the aforesaid degree of unsaturation. The iodine values referred to herein are those determined by the iodine monochloride method described in the British Pharmacopoeia, 1953, pages 754-755.

It has been found, for example, that the presence of finely dispersed metallic sodium in a mineral oil in a proportion amounting to 20 per cent. of the weight of the oil decreases the period of the purification treatment by at least 50 per cent. as compared with the period required for purification with the mineral oil alone.

The finely divided metallic sodium preferably has a particle size not exceeding 150 microns. It is advantageously used in the form of a dispersion in an organic liquid. Such dispersions and methods of preparing them are known, see for example, United States Specifications Nos. 2,394,608, 2,487,333 and 2,487,334. When the organic dispersing medium is capable of undergoing carbonisation when heated in liquid titanium tetrachloride, as in the case of a mineral oil, it may also serve as the carbonisable organic material used in the present process.

Titanium tetrachloride which has been purified by the process of this invention is very suitable for the manufacture of titanium dioxide or metallic titanium or organic compounds of titanium, and as a catalyst in various processes for polymerising organic compounds.

The following Example illustrates the invention:

100 parts by weight of crude liquid titanium tetrachloride containing 0.052 per cent. of vanadium (calculated as  $V_2O_5$ ) were heated at the boil under reflux with 0.14 part by weight of the mineral lubricating oil having an iodine number of 12, and known in commerce as "Vitrea 69" (Registered Trade Mark), in which oil 0.04 part by weight of metallic sodium had been finely dispersed in the form of particles of less than 150 microns by agitating molten sodium with the hot oil

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by means of a high speed stirring device. The refluxing was continued until vanadium could no longer be detected in the vapour above the boiling liquid. The titanium tetrachloride was then distilled off and collected. The purified product contained less than  $1.5 \times 10^{-3}$  per cent. of vanadium (calculated as  $V_2O_5$ ). The refluxing period was 50 minutes.

The above procedure was repeated without the addition of the sodium, and in this case a refluxing period of 135 minutes was required to achieve the same degree of purity.

The procedure described in the first paragraph of the above Example was repeated without the addition of the lubricating oil, and with 0.04 part by weight of metallic sodium alone. The metallic sodium was used in the form of a coating on the particles of dry inert powder. The purification was not complete after refluxing for five hours.

It was also found that traces of impurities, such as chlorine and hydrogen chloride, which were present in some samples of titanium tetrachloride purified by refluxing with the lubricating oil alone, were not present in the samples purified in the presence of the dispersion of sodium in the mineral oil.

The claims defining the invention are as follows:

1. A process for the purification of titanium tetrachloride containing vanadium as an impurity, wherein the impure titanium tetrachloride is heated with a small proportion of carbonisable organic material in the presence of a proportion of finely divided metallic sodium amounting to about 5 to 50 per cent. calculated on the weight of the organic material to bring about carbonisation of the organic material, and the purified titanium tetrachloride is separated from the solid carbonisation products. (25th September, 1956.)

2. A process as claimed in Claim 1, wherein the impure titanium tetrachloride is heated with the organic material and the metallic sodium at a temperature of at least  $100^\circ\text{C}$ . (25th September, 1956.)

3. A process as claimed in Claim 1 or 2, wherein the proportion of the organic material is within the range of 0.1 to 1.0 per cent. calculated on the weight of the impure titanium tetrachloride. (25th September, 1956.)

4. A process as claimed in Claim 1, 2 or 3, wherein the organic material is a carbonisable saturated or unsaturated organic material having an iodine value not exceeding 25. (25th September, 1956.)

5. A process as claimed in Claim 4, wherein the said organic material is a mineral oil. (25th September, 1956.)

6. A process as claimed in Claim 4, wherein the said organic material is a vegetable or animal oil, fat or wax. (25th September, 1956.)

7. A process as claimed in any one of Claims 1-6, wherein the finely divided metallic sodium has a particle size not exceeding 150 microns. (25th September, 1956.)

8. A process as claimed in any one of Claims 1-7, wherein the finely divided metallic sodium is used in the form of a dispersion of the latter in an organic liquid. (25th September, 1956.)

9. A process as claimed in any one of Claims 1-8, wherein the impure titanium tetrachloride is heated in the liquid state with the organic material and the metallic sodium under atmospheric pressure at a temperature within the range of  $100^\circ\text{C}$ . to  $136^\circ\text{C}$ . (25th September, 1956.)

10. A process for the purification of titanium tetrachloride as claimed in Claim 1 and conducted substantially as described in the Example herein. (25th September, 1956.)

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GRIFFITH, HASSEL & FRAZER,  
Patent Attorneys for Applicant.

## References:

Serial No.	Application No.	Classification.
07,659	9809/55	15.6; 08.4
60,108	11,339/52	08.4; 15.6
08,193	11,032/55	08.4

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(19) **United States**(12) **Patent Application Publication** (10) Pub. No.: **US 2001/0016182 A1**  
(43) Pub. Date: **Aug. 23, 2001**  
**Cronin et al.**(54) **PROCESS FOR CONTROLLING THE  
PASSIVATION OF ALUMINUM CHLORIDE  
FORMED IN THE CHLORINATION OF  
TITANIUM-CONTAINING ORES**(21) Appl. No.: **09/739,597**(22) Filed: **Dec. 18, 2000****Related U.S. Application Data**(63) Continuation-in-part of application No. 09/346,410,  
filed on Jul. 1, 1999, now abandoned.**Publication Classification**(51) Int. Cl.<sup>7</sup> ..... **C01G 25/06; C22B 34/10**(52) U.S. Cl. .... **423/82; 423/492**(57) **ABSTRACT**

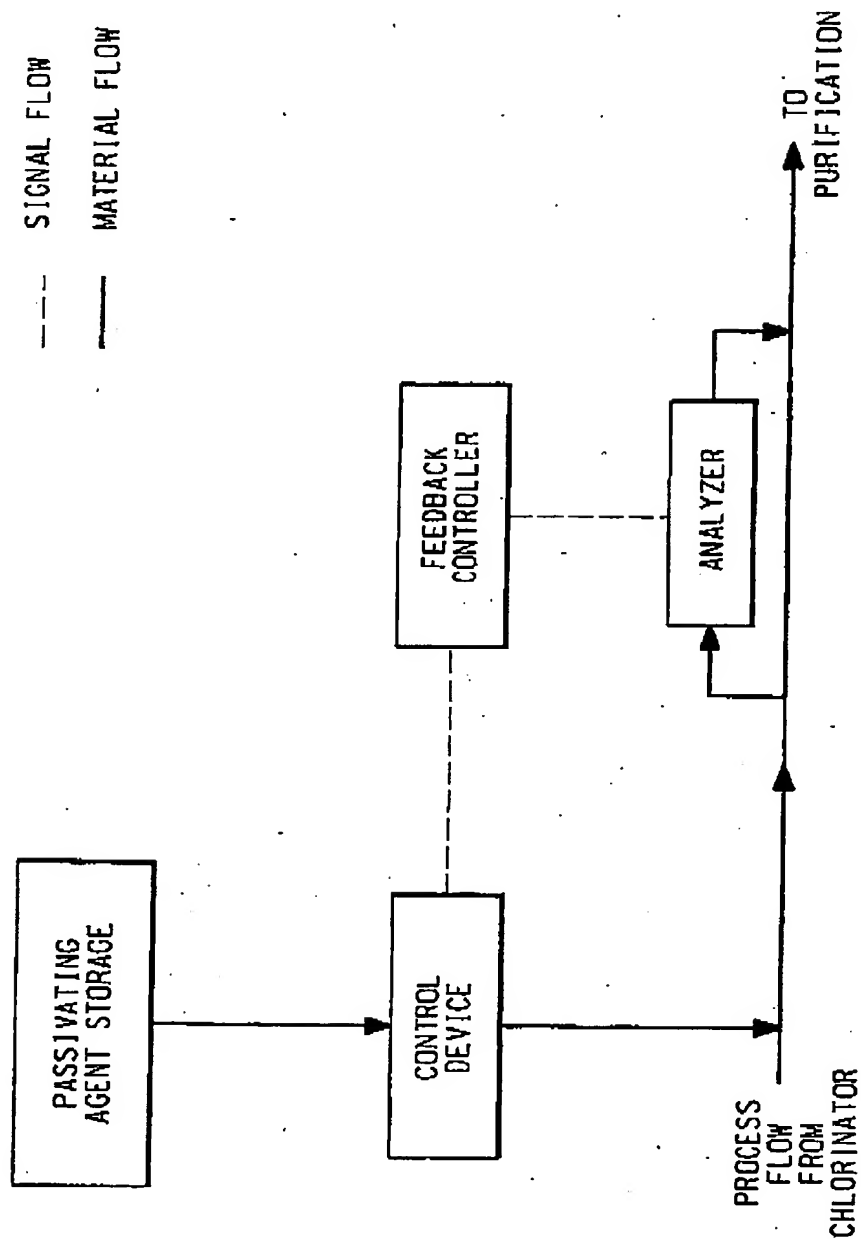
The present invention is a process for controlling, at an aim point, the passivation of aluminum chloride in the chlorinator discharge stream in a process for making titanium tetrachloride.

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FIGURE

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**PROCESS FOR CONTROLLING THE  
PASSIVATION OF ALUMINUM CHLORIDE  
FORMED IN THE CHLORINATION OF  
TITANIUM-CONTAINING ORES**

**BACKGROUND OF THE INVENTION**

[0001] In the production of titanium tetrachloride, raw materials, including ilmenite or rutile ores or other titanium-rich materials such as those obtained from beneficiating these ores, are reacted with chlorine under reducing conditions to yield a mixture of metal chlorides from which titanium tetrachloride may be recovered.

[0002] Aluminum chloride is present in the chlorination product of practically every case where aluminum compounds are present in the raw materials. Aluminum chloride present in the crude titanium tetrachloride is a highly corrosive material. It both quickly and severely attacks the metal materials of construction in the purification systems.

[0003] Prior art has taught methods by which aluminum chloride present in the crude titanium tetrachloride may be passivated, meaning the aluminum chloride is converted to a less corrosive or non-corrosive compound.

[0004] U.S. Pat. No. 2,600,881 to Kay and Rick teaches the addition of water to the crude titanium tetrachloride. According to this patent, water is added in an amount that is sufficient to react with only the aluminum chloride present in the crude titanium tetrachloride. Water reacts with the aluminum chloride and converts it to a less volatile, non-corrosive hydrate or oxychloride. Although this patent teaches a method of passivating the aluminum chloride, there continued to be a major disadvantage. If water was added in excess of that amount just sufficient to remove the aluminum chloride, the excess water reacted with the titanium tetrachloride converting it to hydrolysis products resulting in losses of titanium value. This patent offered no teaching or suggestion as to how to avoid the addition of excess water or how to accommodate the variations in aluminum chloride content of crude titanium tetrachloride that may be experienced in a continuous industrial process.

[0005] It was reported in U.S. Pat. No. 4,125,586 to Glacser that to successfully apply the method taught in U.S. Pat. No. 2,600,881 on a commercial scale required that at least 10% excess water be added in order to effectively passivate the aluminum chloride. As an improvement to reduce losses of titanium value, U.S. Pat. No. 4,125,586 taught that loss in titanium value could be essentially eliminated by adding a mixture of water and sodium chloride to the crude titanium tetrachloride. The water addition was made in an amount less than that needed to convert all the aluminum chloride present to aluminum oxychloride; but the sum of the total amounts of water and sodium chloride added was in excess of that amount needed to react with the aluminum chloride present.

[0006] While U.S. Pat. No. 4,125,586 was an improvement, there was still the need to have a method that could control passivation of aluminum chloride present in the crude titanium tetrachloride at a process aim point reducing both the losses of titanium value and the corrosion.

[0007] U.S. Pat. No. 4,070,252 to Bonsack teaches a method for separating niobium and/or tantalum chlorides from a liquid crude titanium tetrachloride vehicle by adding

water to the crude titanium tetrachloride vehicle in a portion not substantially above 1 mole per mole of these chlorides. Bonsack teaches that the addition of water in his process may be made before or after the chlorination reaction.

[0008] Even in view of the teachings of the art cited above, an accurate, in-process control method was needed that could respond to the demands of continuous plant operation where there are variations in the aluminum chloride content of the crude titanium tetrachloride due to (1) variations in the uniformity in the distribution of the aluminum containing minerals in the ore being processed; (2) variations in the rate at which ore is processed; (3) variations in aluminum content from one ore source to another; (4) variation in the content of mineral species other than those containing aluminum and titanium that consume the passivating agent; and (5) variation in the amount of aluminum chloride removed with any initial separation of higher boiling metal chlorides from the product titanium tetrachloride vapor.

**SUMMARY OF THE INVENTION**

[0009] An in-process, real time control loop capable of controlling the passivation of aluminum chloride formed in the chlorination of titanium-containing ores by monitoring titanium oxychloride present in passivated crude titanium tetrachloride comprising the steps:

[0010] (a) rapidly mixing into a chlorinator discharge stream, where the stream comprises predominately vapor in the presence of liquid mist and solids, an aluminum chloride-passivating agent to form in the process stream an essentially non-corrosive aluminum containing compound, and titanium oxychloride;

[0011] (b) measuring in-process the concentration of titanium oxychloride in the chlorinator discharge stream or in the crude titanium tetrachloride.

[0012] (c) comparing the measured concentration of titanium oxychloride to that of an aim point concentration of titanium oxychloride; and

[0013] (d) adjusting the rate of addition of the aluminum chloride-passivating agent to restore or maintain the concentration of titanium oxychloride at the aim point.

[0014] The aluminum chloride-passivating agent is selected from the group consisting of water, water containing solutions, water containing mixtures, and carboxylic acids.

[0015] In the present process it is preferred to measure the concentration of titanium oxychloride by an optical method selected from the group consisting of transmission filter Infrared spectroscopy, transmission Fourier Transform Infrared spectroscopy, Raman spectroscopy, Attenuated Total Reflectance Infrared spectroscopy, and Attenuated Total Reflectance Fourier Transform Infrared spectroscopy.

[0016] It is also preferred that the measurement of the concentration of titanium oxychloride be made in a frequency range of from 800 to 2000  $\text{cm}^{-1}$ .

[0017] It is most preferred that the concentration of titanium oxychloride is measured by diamond based Attenuated Total Reflectance Fourier Transform Infrared at a frequency of about 820  $\text{cm}^{-1}$ .

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## BRIEF DESCRIPTION OF THE DRAWING

[0018] The FIGURE illustrates a control loop of the present invention.

## DETAILED DESCRIPTION

[0019] The present invention is a process control loop capable of controlling, at an aim point, the passivation of aluminum chloride present in the chlorinator discharge stream in a process for making titanium tetrachloride. The phrase passivation of aluminum chloride as used herein means that the aluminum chloride is converted to a less corrosive or non-corrosive compound. The term "real-time" means actual time when the passivation is taking place in the process. Thus, the in-process, real-time control loop of the present invention provides a way to accurately passivate the corrosive aluminum chloride without the addition of water or another passivating agent in excess of that which is actually required to react with the aluminum chloride present at desired point of passivation.

[0020] The present process requires the addition of the passivating agent into a chlorinator discharge stream where the stream comprises predominately vapor along with liquid mist and solids. It is in this point of the process where mixing is rapid and the desired product selectivity can be achieved. If the addition of the passivating agent, particularly water, were made before the chlorination reaction, as is taught in Bonsack, the water would react with the chlorine and coke to produce hydrogen chloride gas and carbon dioxide destroying the agent. Under these conditions, aluminum chloride formed in the chlorinator would leave the chlorinator as an active (unpassivated) agent causing serious corrosion of equipment.

[0021] On the other hand, addition of the passivation agent down stream and into the chlorinator discharge where the product stream is predominantly liquid may irreversibly produce titanium dioxide. This production of titanium dioxide represents a serious yield loss since it is separated from the titanium tetrachloride product stream along with coke and other waste product solids.

[0022] In the present invention, the point of addition of the passivation agent into the flow of the chlorinator product stream is optimized for (1) the reduction and elimination of corrosion from active aluminum chloride, (1) minimal yield losses of titanium tetrachloride, and (3) in a process stream in real-time.

[0023] The inventors in the present process have found that long exposure of titanium oxychloride in the liquid titanium tetrachloride under conditions, as is suggested by Bonsack and in the article by N. K. Druzhinina entitled Some Studies of the  $AlCl_3-TiCl_4-H_2O$  System in *Tr. Vses. Issled. Alumin-Magnit. Inst.*, no. 50:147-52(1963), produce an inactive titanium oxychloride polymer. That is, a polymer form of titanium oxychloride that does not back react according to the accepted reaction sequence such as is the sequence presented in Bonsack col. 2. The presence of this titanium oxychloride polymer will lead to a false indication in the measuring scheme of the present invention. That is, infrared spectra would record the presence of the titanium oxychloride polymer species at  $820\text{ cm}^{-1}$ , while aluminum chloride is still present as an unpassivated species in the product stream.

[0024] In the present process the aluminum chloride is made non-corrosive by reacting the aluminum chloride containing crude titanium tetrachloride with an aluminum chloride-passivating agent. The term aluminum chloride-passivating agent as used herein means an agent that reacts with the aluminum chloride to form a non-corrosive or essentially non-corrosive aluminum containing compound and also results in the production of titanium oxychloride. Passivating agents include water, water solutions, water containing mixtures, and carboxylic acids. For example, water solutions of sodium chloride or sodium hydroxide or water solutions or mixtures containing carboxylic acids are suitable as passivating agents for the aluminum chloride.

[0025] Although chemical theory offers some guidance in the selection of an aluminum chloride-passivating agent, one may screen passivating agents by adding the material in question, alone or as a solution or mixture in water, to titanium tetrachloride containing a known amount of aluminum chloride to form a treated sample. The concentration of aluminum chloride in the treated sample is then measured to determine the amount of aluminum chloride that has reacted and the amount of titanium oxychloride formed. The reduction in corrosion is determined by comparing the corrosion of the treated sample to that of a control using metal coupons. Selection of a passivating agent may also require such considerations as cost and the material's overall acceptability for an industrial process.

[0026] Water is most preferred as a passivating agent in the present process. Water solutions or mixtures may be used as passivating agents even if the materials other than the water show no reactivity towards the aluminum chloride. To realize the full potential of the present invention, it is clear that one must avoid the use of a material that causes instability (reaction to re-form aluminum chloride) in the non-corrosive aluminum compound formed, that uncontrollably depletes the titanium value of the crude titanium tetrachloride, or produces solid deposits on equipment surfaces.

[0027] The present invention is designed for use in-process. In the present control loop, it is preferred to place the addition of the aluminum chloride-passivating agent as near the point of titanium tetrachloride condensation where the product titanium tetrachloride and other metal chlorides are a mixture of vapor and liquid mist. Addition of the passivating agent at this point in the reaction both minimizes yield losses due to the formation of titanium dioxide and the formation of non-reactive polymer forms of  $TiOCl_2$ .

[0028] Although the mechanism of the reaction is not fully understood, the inventors have found that aluminum chloride is passivated and the extent of the passivation is indirectly indicated, and may be controlled by the monitoring the formation of titanium oxychloride. The inventors have found that when the aluminum chloride-passivation reaction is carried out in a vapor/liquid mist-containing phase with rapid mixing, the passivation rate is rapid—in fact, only limited by the rate of mass transfer—and the formation of titanium dioxide is avoided. Titanium oxychloride formed is a reactive species not a persistent species as long as aluminum chloride is present in the titanium tetrachloride.

[0029] The term chlorinator discharge stream means the product stream of the chlorinator as the streams leaves the

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chlorinator and enters into the titanium tetra condensation section of the process. This term also includes a process stream from the chlorinator where there has been some initial condensation of the higher boiling metal chlorides such as iron chloride. The essential feature of the present invention is that the addition of the passivating agent is made where the physical state of the chlorinator discharge stream is predominately vapor in the presence of liquid mist and solids.

[0030] Under conditions other than those of the present invention, yield losses due to the formation of titanium dioxide and excess titanium oxychloride are much greater, and at the same time there is no assurance that the aluminum chloride has been passivated since such conditions cause the formation of a non-reactive titanium oxychloride polymer species. Under the reaction conditions of the present invention, regardless of the amount of impurities that consume passivating agent, as long as  $\text{TiOCl}_2$  is detected, all of the  $\text{AlCl}_3$  has been passivated.

[0031] According to the process of the present invention, the presence of titanium oxychloride in the process stream indicates that the aluminum chloride has been passivated. Since titanium oxychloride is soluble in titanium tetrachloride at the process conditions that exist in the present process, the concentration of titanium oxychloride provides a means both to monitor and to control aluminum chloride passivation by in-process measurement.

[0032] The formation of titanium oxychloride represents a loss of titanium value; but solubility and detectability of this oxychloride provide a means to control the addition of water or another aluminum chloride-passivating agent to an amount that is only minimally above that required to react with the aluminum chloride. The presence and concentration of titanium oxychloride may be measured by use of transmission filter Infrared spectroscopy, transmission Fourier Transform Infrared spectroscopy, Raman spectroscopy, and Attenuated Total Reflectance Infrared spectroscopy, and Attenuated Total Reflectance Fourier Transform Infrared spectroscopy in a frequency range of from 800 to 2000  $\text{cm}^{-1}$ .

[0033] In the raw process stream from a chlorinator, for example, as much as 10% by weight of the material may be particulate material that scatters or absorbs light. It is recommended to use attenuated reflectance methods for measurements made on the raw process stream where particle concentrations are high. For accuracy and precision, it is most preferred to measure the presence and the concentration of titanium oxychloride by diamond based Attenuated Total Reflectance Fourier Transform Infrared at a frequency of about 820  $\text{cm}^{-1}$ . Diamond based attenuated reflectance means that the infrared probe or detector placed in the process stream has a diamond element. Suitable probe units include those manufactured by ASI Applied Systems of Millersville, Md., Axiom Analytic, Inc. of Irvine, Calif. and others.

[0034] The probe or detector may be located in the immediate vicinity of the addition point for the aluminum chloride-passivating agent or downstream. Its actual location is not critical as long as it is located in an area where the temperature ensures that titanium oxychloride will be in solution. Measurement of the concentration of titanium oxychloride may also be made using transmission methods following the inline filtering or screening out of interfering

particles. In a case where particle concentrations are less than a percent-or-so in the crude titanium tetrachloride, or are due only to the formation of the insoluble hydrolysis products on addition of water or a carboxylic acid; the presence of particles may be accommodated by the use of multiple scan averaging techniques.

[0035] In general the operation of the present invention may be described by the illustrated control loop of the FIGURE. The control loop comprises a control device, a feedback controller, and an analyzer. The analyzer includes the signal generator (frequency range of from 800 to 2000  $\text{cm}^{-1}$ ), and detector. The analyzer measures the concentration of titanium oxychloride downstream from the point of addition of the passivating agent. The analyzer produces an output signal representing the measured concentration of titanium oxychloride. This output signal is sent to the feedback controller. There the concentration of the titanium oxychloride measured by the analyzer is compared to the predetermined aim point. The feedback controller, based on this comparison, provides input to the control device to adjust the addition rate of the passivating agent to restore or maintain the concentration of the titanium oxychloride at the aim point. Algorithms used in the analyzer and the feedback controller to convert the data collected to a signal output are not critical. One skilled in this art can select or design an algorithm suitable to the specific type of analyzer or feedback controller. The control device may be any regulated flow device equipped with an automatic actuator. Typically the control device is a valve.

[0036] The present process allows both to minimize the yield loss of titanium value while at the same time controlling of the passivation of aluminum chloride. By introducing the passivating agent into the chlorinator discharge stream where the stream comprises predominately vapor, liquid mist and solids one can accurately and efficiently control the addition of a passivating agent in real time by monitoring the concentration of titanium oxychloride present in the crude titanium tetrachloride formed on the addition of the passivating agent. The present control loop responds rapidly to variations in the aluminum chloride content of the crude titanium tetrachloride indirectly by comparing the concentration of titanium oxychloride present at a certain time with the concentration selected as the aim point. It is desirable to set the aim point at the lowest reliable concentration of titanium oxychloride that is detected by the analytical detection device used in the control loop. The rate of addition of the passivating agent is automatically adjusted to compensate for any increase or decrease of the titanium oxychloride that results from the increase or decrease in the aluminum chloride present in the crude titanium tetrachloride.

[0037] Any suitable analytical detection method may be used in the present invention. As stated above, it is most preferred to monitor at a frequency of 820  $\text{cm}^{-1}$  using the Fourier Transform infrared method. This provides sensitivity and precision for the in-process measurements in the presence of high concentrations of particles. Using this technique titanium oxychloride in concentrations as low as 0.1% may be reliably measured.

[0038] The control loop of the present invention provides a means to reduce the addition of water or other passivating agents to an amount minimally in excess of that needed to react with all the aluminum chloride present. The resulting



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reductions in corrosion and deposition of aluminum containing solids in the present process are equivalent to methods of the prior art; yet, at the same time, the present process allows real time, on-line process control with controlled addition of water or other aluminum chloride-passivating agent to substantially reduce the loss of titanium value.

[0039] The present invention provides a real-time, in-process passivation control at an aim point. The present control loop that is fast and is responsive to the demands of continuous in-process operation. The control loop responds in real-time to control the addition of the passivating agent where there are variations in the aluminum chloride content of the crude titanium tetrachloride due to (1) variations in the uniformity in the distribution of the aluminum containing minerals in the ore being processed; (2) variations in the rate at which ore is processed; (3) variations in aluminum content from one ore source to another; and (4) variation in the content of mineral species other than those containing aluminum and titanium that consume the passivating agent. The present real-time control loop combined with the location of the addition of the passivating agent minimizes both the losses of titanium value from titanium tetrachloride reaction with excess concentrations of passivating agent and losses of service time from corrosion of equipment and the formation of unwanted deposits.

What is claimed is:

1. An in-process, real-time control loop capable of controlling the passivation of aluminum chloride formed in the chlorination of titanium-containing ores by monitoring titanium oxychloride present in passivated crude titanium tetrachloride comprising the steps:

(a) rapidly mixing into a chlorinator discharge stream, where the stream comprises predominately vapor in the

presence of liquid mist and solids, an aluminum chloride-passivating agent to form in the process stream an essentially non-corrosive aluminum containing compound, and titanium oxychloride;

(b) measuring in-process the concentration of titanium oxychloride in the chlorinator discharge stream or in the crude titanium tetrachloride;

(c) comparing the measured concentration of titanium oxychloride to that of an aim point concentration of titanium oxychloride; and

(d) adjusting the rate of addition of the aluminum chloride-passivating agent to restore or maintain the concentration of titanium oxychloride at the aim point.

2. The process of claim 1 wherein the aluminum chloride-passivating agent is selected from the group consisting of water, water containing solutions, water containing mixtures, and carboxylic acids.

3. The process of claim 1 wherein the concentration of titanium oxychloride is measured by an optical method selected from the group consisting of transmission filter infrared spectroscopy, transmission Fourier Transform Infrared spectroscopy, Raman spectroscopy, and Attenuated Total Reflectance Infrared spectroscopy, and Attenuated Total Reflectance Fourier Transform Infrared spectroscopy.

4. The process of 3 wherein the measurement of the concentration of titanium oxychloride is made with in a frequency range of from 800 to 2000  $\text{cm}^{-1}$ .

5. The process of claims 1 or 3 wherein the concentration of titanium oxychloride is measured by diamond based Attenuated Total Reflectance Fourier Transform Infrared at a frequency of about 820  $\text{cm}^{-1}$ .

\* \* \* \* \*

Patented June 17, 1952

2,600,881

## UNITED STATES PATENT OFFICE

2,600,881

PURIFICATION OF TITANIUM  
TETRACHLORIDE

William Lewis Kay and Christian Edward Rick,  
Wilmington, Del., assignors to E. I. du Pont de  
Nemours & Company, Wilmington, Del., a cor-  
poration of Delaware

No Drawing. Application July 21, 1950,  
Serial No. 175,294

4 Claims. (Cl. 202-57)

This invention relates to the purification of titanium tetrachloride, and more particularly to the removal of aluminum chloride therefrom.

Titanium tetrachloride is produced commercially by chlorinating, under reducing conditions, titaniferous ores such as rutile or ilmenite, or other titanium-rich materials such as those obtained by beneficiating such ores. These raw materials, in addition to their titanium values, contain varying amounts of compounds of other metals. In the chlorination conversion of the titanium and the other metal compounds to their vaporous chlorides occurs, which chlorides are then recovered and condensed to the solid or liquid state depending upon the physical properties of the component and the recovery apparatus resorted to. The crude titanium tetrachloride is usually recovered by condensing it to a liquid sludge, but this crude product is undesirably contaminated with dissolved impurities and undissolved solid materials. The amount and type of chlorides present in the crude liquid naturally depends upon the exact composition of the titaniferous raw material chlorinated and the particular chlorination method resorted to. The presence of aluminum chloride is to be expected in practically all cases where aluminum compounds are present in the raw materials.

The removal of aluminum chloride and other contaminating chloride compounds comprises a major obstacle in the efforts being constantly made to obtain titanium tetrachloride in a pure, water-white state. The most usual purification procedure is to subject the crude liquid to distillation to separate out a number of its less volatile components. Aluminum chloride removal can be effected to a fairly adequate extent, provided use of an efficient rectification system is also resorted to. However, a serious disadvantage attends the use of this method which heretofore has been impossible to overcome. This arises from the fact that the aluminum compound present in the crude  $TiCl_4$  is highly corrosive, and disadvantageously quickly and severely attacks metallic materials of construction in the purification apparatus. Consequently, the costs of maintenance and replacement of metal distillation and other purification equipment in such instances are extremely and prohibitively high. On the other hand, purified  $TiCl_4$ , or even  $TiCl_4$  containing various other impurities but not active aluminum chloride, is relatively non-corrosive. These facts are graphically illustrated by the following results from tests on mild steel and of nickel equipment, wherein penetration or cor-

rosion was measured in terms of inches per month on apparatus employed to distill pure  $TiCl_4$ ,  $TiCl_4$  containing active  $AlCl_3$ , and  $TiCl_4$  containing hydrated  $AlCl_3$ , respectively:

	Inches/Month Penetration	
	Mild Steel	Nickel
Pure $TiCl_4$ +2% $AlCl_3$ (active)	.00814	.00350
Pure $TiCl_4$ +2% $AlCl_3$ (as $AlCl_3 \cdot 6H_2O$ )	.00622	.00017
Pure $TiCl_4$	.00655	.00016

It is among the objects of this invention to overcome the disadvantages accompanying prior methods for purifying impurity-contaminated titanium tetrachloride; and, in particular, to minimize substantially or prevent the corrosion problems heretofore encountered in processing crude titanium tetrachloride containing active aluminum chloride. A particular object is to provide a novel method for processing  $TiCl_4$  wherein metal equipment can be utilized and with a minimum of maintenance and replacement expense. Another object is to effect removal of aluminum chloride from its solution in liquid titanium tetrachloride, such as that derived from the chlorination of a titaniferous ore or other raw material, and through a relatively simple and inexpensive purification procedure. Other objects and advantages of the invention will be apparent from the ensuing description thereof.

These and other objects are attained in this invention, which broadly comprises mixing with aluminum chloride-contaminated liquid titanium tetrachloride an amount of water substantially stoichiometrically equivalent to the aluminum chloride to be inactivated in said liquid and then separating the resulting aluminum chloride complex from the titanium tetrachloride to recover the latter.

In a more specific and preferred embodiment, the invention comprises subjecting liquid titanium tetrachloride, contaminated with chlorides of aluminum and other metals, to treatment with water in an amount chemically equivalent to the aluminum chloride to be removed or inactivated, and then distilling the resulting mass to vaporize and separately recover the  $TiCl_4$  present in pure form and retain the resulting aluminum chloride complex and other chlorides less volatile than the  $TiCl_4$  as residue in the distillation vessel.

One particularly valuable adaptation of the present process involves the preparation of pure,

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water-white titanium tetrachloride from the conventional chlorination, under reducing conditions, of titaniferous raw material such as an ore or a slag. Such raw material is chlorinated at elevated temperatures and in accordance with, for instance, the procedures of U. S. Patents 2,184,885, 2,184,887, 2,245,076, etc., whereby a vaporous mixture of titanium, aluminum and other chlorides is obtained. Upon condensation and recovery of the crude titanium tetrachloride product, the condensate is analyzed to determine its aluminum chloride content. A quantity of water is then mixed with the  $TiCl_4$  sufficient only to react with the active aluminum chloride present therein, as a result of which the aluminum chloride appears to react selectively with the water and form in situ of the  $TiCl_4$  a complex hydrate or oxychloride of low volatility, non-corrosive, and relatively inactive chemically. The resulting mass or mixture is thereafter subjected to distillation to effect volatilization and removal of the  $TiCl_4$  for separate recovery through condensation, while the aluminum chloride complex, being less volatile, remains in the distillation vessel. Due to the inactive and essentially non-corrosive nature of this complex, undesired wear or corrosive attack of equipment is materially lessened or completely obviated, and recovery is thereby afforded of a  $TiCl_4$  fraction substantially free of active aluminum and other less volatile contaminating chlorides.

To a clearer understanding of the invention, the following illustrative examples are given which are not to be considered as limiting its scope:

#### Example I

Minerite ore was mixed with coke and chlorinated with  $Cl_2$  gas at about 950° C. The product vapors comprising titanium and other metal chlorides were cooled and crude  $TiCl_4$  condensed to liquid form was subsequently recovered therefrom. This liquid comprised principally  $TiCl_4$  with contaminating chlorides, particularly 0.55% by weight of active  $AlCl_3$  and 0.15%  $VOCl_3$ .

The crude  $TiCl_4$  was then introduced into an externally-heated distillation vessel provided with conventional agitating and associated condensing means. Liquid water in an amount equivalent to 3 parts by weight of water for 8700 parts by weight of the crude mass was then added to the liquid crude. (On a molar basis, this comprises sufficient water to react chemically with 46.5% of the active  $AlCl_3$ .) Water addition was effected dropwise with constant agitation and upon completion of the addition, the resulting mixture was gradually heated to about 137° C. The heating and resulting boiling operation was continued until the volume of liquid in the vessel became decreased to about one-half. Meanwhile, the vaporous  $TiCl_4$  fraction volatilized and distilled off during the heating was removed and separately recovered. The residue remaining in the vessel following the distillation was analyzed and found to contain an active  $AlCl_3$  content of 0.23% by weight of the original crude material. In other words, 49% of the original  $AlCl_3$  had been reacted with the water to form a non-volatile complex, while 51% remained unreacted. The water added was chemically equivalent to 46.5% of the aluminum chloride in the  $TiCl_4$  and was effectively useful in removing 49% of the aluminum compound. This is considered an experimental verification of the theory that one mol of  $H_2O$  renders one mol of  $AlCl_3$  inactive and non-volatile.

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#### Example II

Another sample of the crude  $TiCl_4$  obtained by the chlorination procedure described in Example I was mixed with water, utilizing the same distilling equipment and the procedures of that example were repeated. In this instance, twice as much water was introduced, i. e., an amount of water stoichiometrically equivalent to an  $AlCl_3$  content of 0.50% by weight was used. The  $TiCl_4$  distillate fraction recovered had a yellowish discoloration due to vanadium presence, and on being analyzed for aluminum chloride, had an active  $AlCl_3$  content of less than 0.08%, indicating that essentially all of the original  $AlCl_3$  had been rendered non-volatile and inactivated by the added water.

The procedure above was repeated, but the water was added after heating of the crude  $TiCl_4$  had been begun and while the temperature of the latter was about 90° C. On analysis the  $TiCl_4$  distillate contained 0.05%  $AlCl_3$ . A water-white product was obtained after refluxing the distillate in the presence of copper and redistilling.

#### Example III

The procedure and crude  $TiCl_4$  of Example I were again employed but the quantity of added water was increased to that stoichiometrically equivalent to an active aluminum chloride content of 1.0% by weight in the titanium chloride. The  $TiCl_4$  distillate recovered analyzed 0.01%  $AlCl_3$ . This product which was substantially free of aluminum chloride like the products of Examples I and II, contained approximately the same vanadium concentration and was discolored by this impurity. Vanadium chloride removal was effected by reheating the distillate after the addition of finely-divided copper and subsequently re-distilling, and a water-white titanium tetrachloride product was obtained.

#### Example IV

Samples of iron and nickel sheet metal were also tested for corrosion or penetration utilizing various  $TiCl_4$  solutions, by boiling the metals for six hours in the solutions. In similar tests, the resistance of the metals to various  $TiCl_4$  vapors was studied. Penetration in inches per month was calculated by the equation:

$$P = \frac{30 \times Z^4}{6} \times \frac{\text{sample weight loss, grams}}{\text{metal density} \times \text{cm}^2 \text{ area of sample} \times 2.54}$$

Results from these corrosion or penetration tests were as follows:

Solution	Penetration in./mo.			
	In Liquid		In Vapor	
	Fe	Ni	Fe	Ni
(1) $TiCl_4$ Pure	.0001	.0001	.0001	.0003
(2) $TiCl_4$ + 1% $AlCl_3$ + $H_2O$	.0001	.0001	.0001	.0003
(3) $TiCl_4$ + 1% $AlCl_3$	.0035	.0020	.0010	.0004

<sup>1</sup> Water added was equivalent chemically to 1%  $AlCl_3$ .

The exact nature of the chemical reaction which occurs by means of the new pre-distillation technique herein contemplated, and the reason for the efficacy of water at this early step in the purification process are not presently well understood. One theory which appears to particularly commend itself is that, following addition of the water to the titanium tetrachloride, a reaction takes place according to the equation:

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$\text{AlCl}_3 + \text{H}_2\text{O} = \text{AlOCl} + 2\text{HCl}$ . The aluminum chloride has a greater affinity for water than have the other components of the crude  $\text{TiCl}_4$  product, so that it is on this material, quite surprisingly, that the water has the desired and selective effect. It may be, however, that the water first reacts with  $\text{TiCl}_4$  to give soluble  $\text{TiOCl}_2$  or another oxychloride compound and that this then reacts with  $\text{AlCl}_3$  upon contact with this solute. Since it is  $\text{AlCl}_3$  which is chemically active and therefore is the principal cause of metal surface corrosion, while aluminum oxychlorides, hydrates and the like are relatively inactive and non-volatile under the conditions obtaining in the usual  $\text{TiCl}_4$  purification, it will be readily seen that the addition of water at this preliminary stage in the operation, as herein contemplated, simply and effectively inhibits the serious corrosion problem heretofore encountered. The above equation indicates that equimolar proportions of aluminum chloride and water are all that are necessary, and this observation has been borne out in practice. In general, one mol of water should be added for each mol of aluminum chloride to be removed from the crude  $\text{TiCl}_4$ . While a lesser amount can be used, since it will prove valuable in removing at least some of the  $\text{AlCl}_3$  and hence lessen equipment corrosion to that extent, it will be found preferable to inactivate essentially all of the  $\text{AlCl}_3$ , and to utilize for that purpose a mol for mol treatment. As already noted, the use of excess water is undesirable because loss of titanium values will occur due to formation of titanium oxychlorides and the like, when active  $\text{AlCl}_3$  is no longer present to react selectively with the water.

The method of incorporating the required amount of water in the crude tetrachloride is relatively unimportant, so long as an intimate mixture is obtained. The water may be added to the  $\text{TiCl}_4$  by merely dropping or otherwise feeding it onto the surface of the latter, or, if preferred, can be injected into the liquid, or otherwise commingled therewith by any known and desired means. Similarly, intimate admixture can be effected through resort to any common means, such as mechanical agitation with a paddle, circulation pump, or similar media. The time required to effectuate adequate mixing and treatment appears to depend upon the efficiency of the mixing operation rather than upon the speed of chemical reaction. The temperature of the crude product in which the water is commingled is also relatively unimportant, and in the subsequent heating to effect distillation, temperatures which at least approximate the boiling point of the  $\text{TiCl}_4$  component are resorted to. Advantageously, water addition to the condensate ( $\text{TiCl}_4$ ) is effected as the latter is collected, to render the crude  $\text{TiCl}_4$  non-corrosive as soon as possible, and preferably at the temperature of the condensed  $\text{TiCl}_4$  as formed. The term "water" includes free water in the vapor, liquid, or solid (ice) state.

As will be evident from the foregoing, the present invention provides a novel, efficacious and surprisingly simple method for initially treating crude titanium tetrachloride containing aluminum chlorides and other impurities to effectively minimize the corrosion of metal purification equipment so disadvantageous up to now, and enable ultimate recovery of a water-white product. By its use, purification of  $\text{TiCl}_4$  derived from chlorination of a titaniferous ore or slag is made relatively simple and inexpensive, and

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distillation may now be effected readily and efficiently. This is achieved by introducing a new step into the usual purification process, after or during the condensation of the crude  $\text{TiCl}_4$  product and before distillation, the addition of which step actually, and unexpectedly, reduces in a startling manner the costs of the purifying operation.

The process outlined is particularly useful in the conversion of impure liquid titanium tetrachloride to the purified water-white product. Water addition to the crude product, in the amounts specified, of itself does not provide a water-white product nor reduce the vanadium content of the titanium compound upon subsequent distillation. It is believed that the water simply functions to render the aluminum chloride solute inactive and less volatile by converting it to an oxychloride, such as  $\text{AlOCl}$ . The inactivated aluminum compound is also soluble in the  $\text{TiCl}_4$  under the conditions of its preparation; but the corrosiveness of the liquid is materially decreased and may be handled in standard iron and nickel equipment without impairing the life of the equipment. Upon distillation, the aluminum compound remains in the distillation vessel as residue while the more volatile titanium chloride is separated therefrom along with impurities of similar volatility such as vanadium oxychloride  $\text{VOCl}_3$ . Freeing the titanium tetrachloride from volatile color-imparting impurities such as a chloride of vanadium is then conventionally effected by an additional treatment such as by distillation over a copper contact mass.

Titanium tetrachloride obtained from the chlorination of titanium ores forms a crude product of commerce having the following composition:

	Per cent
$\text{TiCl}_4$ .....	95
$\text{Cl}_2$ .....	2.0
$\text{AlCl}_3$ .....	0.5
$\text{FeCl}_3$ .....	0.5
$\text{SbCl}_3$ .....	0.7
$\text{SiCl}_4$ .....	0.4
$\text{SnCl}_4$ .....	0.05
$\text{VOCl}_3$ .....	0.15
$\text{CO}_2$ .....	trace
$\text{CO}$ .....	trace
$\text{COCl}$ .....	trace
$\text{HCl}$ .....	trace

In accordance with the invention, it will be found advantageous to incorporate therein an amount of water up to the quantity of aluminum chloride present immediately after its condensation and segregation, so that the life of the equipment will thereby be advantageously increased. It has also been found that water addition decreases the electrical conductivity of the titanium tetrachloride product containing a small amount of  $\text{AlCl}_3$ . It appears that this increased conductivity of the solution of aluminum chloride in  $\text{TiCl}_4$  is related in some way with corrosiveness. By the water treatment herein contemplated, a method is provided for decreasing the conductivity and thereby the corrosiveness of the chemical.

In the specification reference has been made to the inactivation of aluminum chloride by the addition of water. It is understood thereby that aluminum, when present as dissolved  $\text{AlCl}_3$ , is considered to be "active" and that when present as  $\text{AlOCl}$ , it is "inactive." Crude  $\text{TiCl}_4$  may

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contain aluminum in both forms and accordingly it will be found to be advantageous to determine the amount of water necessary to react with the active aluminum to convert it to the inactive condition. When water in excess of that amount is used, titanium oxychloride is produced with consequent loss of the chemical being purified or treated. To avoid this, it will be found desirable to employ only such amount of water as is substantially equivalent to the aluminum chloride being inactivated.

We claim as our invention:

1. A process for the removal of aluminum chloride in solution with liquid titanium tetrachloride which comprises mixing with said liquid an amount of water sufficient only to react with the active aluminum chloride to be removed therefrom, and then separating the titanium tetrachloride from the resulting aluminum chloride complex.

2. A process for the removal of aluminum chloride contaminant from liquid titanium tetrachloride which comprises incorporating in the tetrachloride about one mol of water for each mol of aluminum chloride present therein, and then subjecting the resulting mass to distillation to separate the titanium tetrachloride from the residual contaminants.

3. A process for purifying titanium tetrachloride obtained from the chlorination of a titaniferous material to remove aluminum chloride

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contaminant therefrom which comprises adding to said tetrachloride one mol of water for each mol of aluminum chloride present, distilling the mass to separate out the less volatile chlorides, and recovering pure titanium tetrachloride from the titanium tetrachloride fraction.

4. An improved process for the production of purified  $TiCl_4$  from impure  $TiCl_4$  containing as impurities aluminum and vanadium chlorides which comprises rendering the aluminum chloride inactive and non-volatile by adding thereto one mol of water for each mol of the  $AlCl_3$  present, distilling the resulting product to obtain a discolored vanadium-containing distillate, and then refluxing said distillate in the presence of copper as a contact mass.

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April 8, 1952

W. FREY ET AL  
METHOD FOR PURIFYING NORMALLY LIQUID CHLORIDES  
OF METALS OF GROUP 4 OF THE PERIODIC SYSTEM  
Filed July 14, 1948

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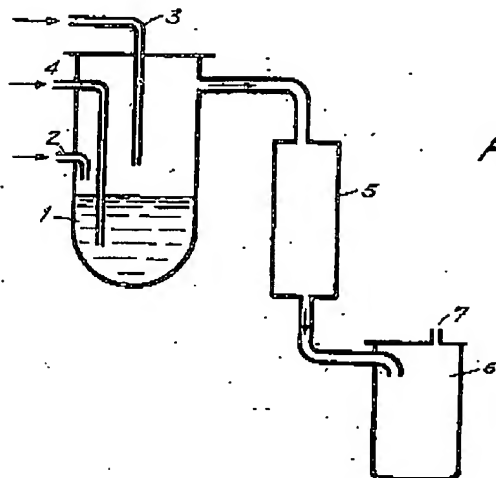


Fig. 1

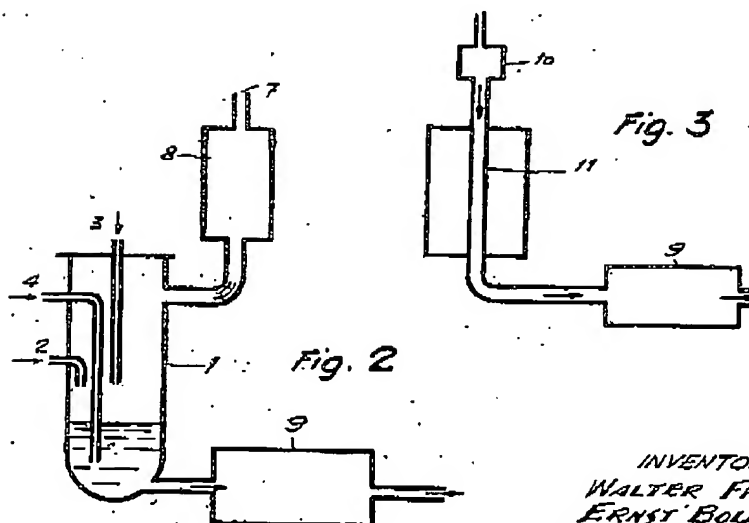


Fig. 2

Fig. 3

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## UNITED STATES PATENT OFFICE

2,592,021

METHOD FOR PURIFYING NORMALLY  
LIQUID CHLORIDES OF METALS OF  
GROUP 4 OF THE PERIODIC SYSTEM

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In Switzerland July 26, 1947

12 Claims. (Cl. 23-87)

**1**  
This invention relates to a method of purifying liquid chlorides of metals of the 4th group of the periodic system. As is well known, the 4th group of the periodic system comprises the elements C, Si, Ti, Zr, Hf, Th, Ge, Sn and Pb.

These metal chlorides are obtained after known methods by direct chlorination of the respective metals, alloys, oxides or oxide ores and owing to the impurities contained in the initial products, they are always impurified by other volatile metal chlorides. The metal chlorides which are solid at normal temperature, such as trichloride of iron, are not soluble or only difficultly soluble in the liquid chlorides. On the other hand, the liquid metal chlorides, such as tetrachloride of vanadium, oxychloride of vanadium and chromylchloride, are completely soluble in the four-valent liquid chlorides, causing the undesirable colouring of the four-valent chlorides which in their pure condition are colourless. Thus, for instance, by chlorinating rutile which always contains up to 1 percent of vanadium oxide and up to 0.5 percent of chromium oxide, a titanium chloride is obtained which contains 0.7 to 0.8 percent vanadium oxychloride and vanadium tetrachloride and up to 0.1 percent chromium oxychloride and, therefore, is of a dark yellow colour. When chlorinating kieselguhr, there is obtained a bright yellow silicon tetrachloride by small quantities (less than 0.1 percent) of vanadium oxychloride. The present process primarily relates to the purification of the liquid four-valent chlorides to eliminate these liquid coloured chlorides.

Simple distillation or even a carefully executed fractional distillation of the coloured metal chlorides would not produce the desired result, since the boiling points of the coloured and of the colourless chlorides are too close together. Now, it is known to effect the purification by absorption of the coloured chlorides on active carbon, silicagel etc. in a liquid or vaporized condition, or to convert the coloured, volatile chlorides at a higher temperature, by means of hydrogen, into non-volatile chlorides, and thus to separate them from the colourless chlorides. Also it has been suggested to treat the raw chlorides in a liquid state with substances such as sulphur, soap, or with metal powders in the presence of alkalis, whereby the coloured chlo-

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rides are converted by reactions which partly are unknown, into non-volatile compounds, so that a chloride which is free from foreign metal chlorides may be distilled off.

Now, it has been found that the purification of the metal chlorides of the fourth group from the coloured metal chlorides can be effected more easily and cheaply in such a way that the chlorides are treated at a higher temperature with organic compounds, preferably used in small quantities, which have no metal attached to the molecule, under such conditions that these organic compounds are carbonized by the chlorides, whereupon the metal chloride freed from the colored chlorides is separated from the eliminated product of carbonization containing the impurities.

As a purifying agent, there may be used, e. g. liquid or vaporous or gaseous hydrocarbons, oils and fats, alcohols, ketones, organic acids, amines and the like. Especially hydrocarbons with at least 2 C atoms and organic compounds containing besides hydrogen at least one activating substituent such as a hydroxyl-, oxy-, keto-, amino- or/and carboxyl group or mixtures containing such substances proved to be suitable.

The organic substances show a different activity as regards purification, depending on their constitution. Therefore, the conditions of the treatment, especially the temperature and pressure conditions, must be adapted to the purifying agent in question. Organic, animal or vegetable fats and oils, especially those with unsaturated combinations, moreover unsaturated hydrocarbons with at least 4 C atoms, also for instance in the form of cracking gases, unsaturated mineral oils, crude oil and benzene are particularly capable of reaction. With these substances in general a reaction temperature of 100-200° centigrade is sufficient. The vegetable and animal fats and oils are referred to hereinafter as fatty oil substances.

Other organic substances, such as for example low molecular, saturated hydrocarbons, aromatic hydrocarbons, alcohols etc. often-times are less capable of reaction and require a higher reaction temperature of 200 to 500° C. When using such purifying agents, therefore, it may be necessary to carry out the purification process under pressure, by heating the mixture or the



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solution, consisting of metal chloride and purifying agents, to the reaction temperature in autoclaves. The purification under pressure is advantageous especially also where silicon chloride is to be purified, for its boiling point is so low that the treatment at normal pressure would take a long time even when using very active purifying agents. By applying higher temperature such as attainable with higher pressure the duration of the treatment can be considerably shortened. The purification by means of gaseous organic substances can be carried out in such a way that the gaseous purifying agent is passed through the metal chloride which is preferably at boiling temperature, at normal or increased pressure.

The manner of action of my novel purifying process probably is due to the fact that the finely-dispersed carbon resulting from the carbonisation process has a very high absorption capacity especially for the colored liquid chlorides.

Our novel method offers the advantage that very cheap purifying agents, such as petrol, crude oil, benzene, liquid paraffin, cracking gases, animal and vegetable fats and oils etc. can be used. Also it is easy to be carried out technically, since the elaborate stirring operation required when using solid purifying agents, such as soap, sulfur and metal powder, can be avoided by using as purifying agents either liquid substances which are partly or wholly soluble in the metal chlorides, such as petrol, benzene and certain mineral oils, or by operating with gaseous purifying agents. The agitation attainable by heating, especially by boiling of the metal chloride, or by introducing a gas, is sufficient for a satisfactory dispersion of the purifying agent in the metal chloride.

Moreover, the purifying operation may be carried out in the form of a continuous process by evaporating the metal chloride to be purified from a still, feeding continuously besides the metal chloride a small quantity of a liquid or gaseous purifying agent, removing continuously or in batches a part, or the whole contents of the still, separating the eliminated, carbonized residue from the liquid, by filtration, and advantageously returning the latter to the still. It will be seen from the examples hereinafter set forth that the contents of colored chlorides can be removed practically completely with minimum losses in colorless metal chloride. The metal chlorides thus purified can be used directly as initial materials for the production of absolutely white pigment colors, such as, for instance, titanium oxide.

A wide variety of different apparatuses can be used for carrying out our novel method, the selection of the most suitable apparatus depending on the conditions of the treatment and the separating methods. When carrying out the method in batches, the apparatus may consist of a still with cooler and adapter or filter, or, in the case of working under pressure, of a stationary or rotary autoclave, combined with a filter or a still pipe with cooler or adapter. For continuous operation the apparatuses shown schematically in the accompanying drawings may be used, in which:

Fig. 1 is a diagrammatic sectional view of a first embodiment;

Fig. 2 is a similar view, showing a second embodiment, and

Fig. 3 is a diagrammatic sectional view showing a third embodiment.

Referring now to the drawings in greater detail,

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and first to Fig. 1 it will be seen that the purifying apparatus consists of a still 1 with feed duct 2 for the chloride to be purified, a feed pipe 3 for the liquid purifying agent, a feed pipe 4 for a gaseous purifying agent, a cooler 5 for condensation of the pure chloride and a recipient vessel 6 provided with a vent pipe 7.

The apparatus according to Fig. 2 consists of a still 1, a return cooler 8, provided with a vent pipe 7, and a filter 9 for filtration of the treated liquid chloride. The devices according to Figs. 1 and 2 may be operated at normal or increased pressure.

The device shown in Fig. 3 consists of a pump 10 by which the mixture, advantageously the solution, of the chloride and the purifying agent is forced into the pressure pipe 11 which is heated from outside. Connected to the pressure pipe is a filter 9 for removing the carbonisation product. Particularly adapted for the filtering operation are ceramic filters, e. g. porous filter plates or filter presses and suction filters with filter cloth of glass or quartz thread.

Some examples of our novel process will now be described.

*Example 1.*—200 grams of titanium chloride, impurified by 2 grams of vanadium chloride, are mixed with 2 grams of linseed oil, boiled for half an hour, and then the titanium chloride is distilled off. A product as clear as water will be obtained with less than 0.01 percent by weight of vanadium. From the same vessel another 7 exactly similar charges with the same admixture of linseed oil are heated and distilled, with the result that a distillate free from vanadium will always be obtained. After the last distillation the carbon-like residue of all the 8 distillations will be removed from the flask and examined; they will contain all the vanadium and 10 grams of titanium chloride so that the loss in titanium chloride is only 0.7 percent.

*Example 2.*—500 grams of tin tetrachloride, impurified by 2.5 grams of vanadium chloride, are boiled with 5 grams of diesel oil for a period of 2 hours and then distilled. The distillate will contain less than 0.01 percent of vanadium.

*Example 3.*—100 grams of silicon chloride, impurified with 0.1 percent of vanadium chloride, are boiled for one hour with 0.1 gram of castor oil under pressure at 150° C. and distilled. The condensation product will contain less than 0.01 percent vanadium.

*Example 4.*—200 grams of titanium chloride impurified with 2 grams of vanadium chloride are boiled for a period of 2 hours with 2 grams of crude petroleum and distilled. The distillate will contain about 0.05 percent of vanadium. To the carbonized residue a second charge of an equal amount is added, also impurified with 2 grams of vanadium chloride, with another addition of 2 grams of crude petroleum, and distilled after 2 hours of boiling, with the result that the distillate will contain less than 0.01 percent of vanadium.

*Example 5.*—200 grams of titanium chloride impurified with 1.5 grams of vanadium chloride are boiled with 2 grams of pulverulent anthracene and then distilled. No vanadium will be found left in the condensed titanium chloride.

*Example 6.*—200 grams of titanium chloride impurified with 2.5 grams of vanadium chloride are boiled for 2 hours with watchmaker's oil, the residue is filtered off after the boiling and a clear titanium chloride, but dark-colored by organic decomposition products, with less than 0.01 percent of vanadium, will be obtained.



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*Example 7.*—A continuously operating distilling apparatus with a still capacity of 600 cubic centimeters is fed with titanium chloride impurified with 1 percent vanadium chloride and 0.3 percent of chromyl chloride, and with cylinder oil, in a ratio of 200:1 at a speed of 900 grams titanium chloride per hour, obtaining a titanium chloride distillate with less than 0.01 percent vanadium and 0.005 percent chromium. After 10 hours of operation the contents of the still is filtered, returning the filtrate to the still which then is ready again for a new operating period of 10 hours.

*Example 8.*—A weak current of amylene (C<sub>5</sub>H<sub>10</sub>) is passed through boiling titanium chloride containing 1 percent vanadium chloride, causing the precipitation of a solid carbonization product. After distilling off from the residue the chloride contains less than 0.01 percent vanadium chloride.

*Example 9.*—Stannic chloride, impurified with 0.2 percent of vanadium chloride, is saturated with propylene in an autoclave at a pressure of 9 atmospheres, then heated to 350° C. and distilled off. The condensate is vanadium-free.

*Example 10.*—5 grams of pentane are dissolved in 200 grams of titanium chloride which is impurified with 2 grams of vanadium chloride, and the mixture is passed continuously in a liquid state through a pressure pipe at 300° C. and 30 atmospheres. The still hot reaction mixture is filtered through a ceramic filter. The filtered titanium chloride contains less than 0.01 percent vanadium.

*Example 11.*—200 grams of silicon chloride, impurified with 0.1 percent of vanadium chloride, are heated with 5 grams of benzol for one hour to 300° C. in an autoclave, reaching a pressure of 80 atmospheres. The silicon chloride is distilled off and contains less than 0.01 percent vanadium.

*Example 12.*—200 grams of stannic chloride, impurified with 0.5 percent of vanadium chloride, are heated with 10 grams of benzene for one hour to 300° C. at a pressure of 30 atmospheres in a rotary autoclave and then distilled off from the autoclave. The distillate is vanadium-free.

A number of purifying agents which may be used in connection with our novel process, and the most favorable temperatures for treatment therewith will be specified hereinafter.

#### GROUP I

*Purifying agents with an optimum purifying temperature of 100 to 200° C.*

Dipentene, amylene, allyl alcohol, acetone, diisobutylketone, tertiary amyl alcohol, anthracene, benzocatechine,  $\alpha$ -naphthol,  $\beta$ -naphthylamine, cyclohexanone, cyclohexanol, furfural, linseed oil, castor oil, salad oil, cylinder oil, engine oil, watchmaker's oil, anthracene oil, crude oil, petrol, benzene.

#### GROUP II

*Purifying agents with optimum purifying temperature from 200 to 300° C.*

Liquid paraffin, heptyl alcohol, cetyl alcohol, diethylamine, naphthalene, phenylacetic acid, o-aminophenol.

#### GROUP III

*Purifying agents with optimum purifying temperature from 300 to 500° C.*

Ethylene, acetylene, propylene, propane, pentane, benzol, toluol, urea, dicyandiamid, methyl alcohol, glycerine, ethyl alcohol.

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While we have described what we believe to be a preferred form of carrying out our novel process, we would have it understood that we do not limit ourselves to the precise details set forth, but consider ourselves at liberty to make such changes and alterations as fairly fall within the spirit and scope of the invention.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A process for removing coloring impurities from an impure normally liquid chloride of a metal of group 4 of the periodic system which comprises intermixing said chloride and a small proportion of an organic compound selected from the group consisting of hydrocarbons and compounds of carbon, hydrogen and at least one substituent from the group consisting of hydroxy, oxy, keto, amino and carboxyl radicals, heating said organic compound in a liquid body of said chloride at a temperature between 100° and 500° C. at which said compound carbonizes therein until a finely dispersed carbonization product is formed and until said impurities are taken up by said carbonization product, and separating purified metal chloride from said carbonization product holding said impurities.

2. A process for removing coloring impurities from an impure normally liquid chloride of a metal of group 4 of the periodic system which comprises intermixing said chloride and a small proportion of an organic compound selected from the group consisting of hydrocarbons and compounds of carbon, hydrogen and at least one substituent from the group consisting of hydroxy, oxy, keto, amino and carboxyl radicals, heating said organic compound in a liquid body of said chloride under superatmospheric pressure and at a temperature between 100° and 500° C. at which said compound carbonizes therein until a finely dispersed carbonization product is formed and until said impurities are taken up by said carbonization product, and separating purified metal chloride from said carbonization product holding said impurities.

3. A process for removing coloring impurities from an impure normally liquid chloride of a metal of group 4 of the periodic system which comprises intermixing said chloride and a small proportion of an organic compound selected from the group consisting of unsaturated fats and oils and unsaturated hydrocarbons containing at least 4 carbon atoms, heating said organic compound in a liquid body of said chloride at a temperature between 100° to 200° C. at which said compound carbonizes therein until a finely dispersed carbonization product is formed and until said impurities are taken up by said carbonization product, and separating purified metal chloride from said carbonization product holding said impurities.

4. A process for removing coloring impurities from an impure normally liquid chloride of a metal of group 4 of the periodic system which comprises intermixing said chloride and a small proportion of an organic compound selected from the group consisting of saturated hydrocarbons, aromatic hydrocarbons, alcohols, ketones, organic acids and amines, heating said organic compound in a liquid body of said chloride at a temperature between 200° and 500° C. at which said compound carbonizes therein until a finely dispersed carbonization product is formed and until said impurities are taken up by said carbonization product, and separating purified metal chloride from said carbonization product holding said impurities.

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ride from said carbonization product holding said impurities.

5. A process for removing coloring impurities from an impure normally liquid chloride of a metal of group 4 of the periodic system which comprises intermixing said chloride and a small proportion of an organic compound selected from the group consisting of saturated hydrocarbons, aromatic hydrocarbons, alcohols, ketones, organic acids and amines, heating said organic compound in a liquid body of said chloride under super-atmospheric pressure and at a temperature between 200° and 500° C. at which said compound carbonizes therein until a finely dispersed carbonization product is formed and until said impurities are taken up by said carbonization product, and separating purified metal chloride from said carbonization product holding said impurities.

6. A process for removing coloring impurities from an impure normally liquid chloride of a metal of group 4 of the periodic system which comprises introducing into a liquid body of said chloride a small proportion of a compound selected from the group consisting of gaseous hydrocarbons and gaseous compounds of carbon, hydrogen and at least one substituent from the group consisting of hydroxy, oxy, keto, amino and carboxyl radicals, heating said organic compound in said liquid body at boiling temperatures between 100° and 500° C. at which said compound carbonizes therein and a finely dispersed carbonization product is formed and until said impurities are taken up by said carbonization product, and separating purified metal chloride from said carbonization product holding said impurities.

7. A process for removing coloring impurities from an impure normally liquid chloride of a metal of group 4 of the periodic system which comprises dissolving in a liquid body of said chloride a small proportion of a liquid organic compound soluble therein selected from the group consisting of liquid hydrocarbons soluble therein and a likewise soluble compound of carbon, hydrogen and at least one substituent of the group consisting of hydroxy, oxy, keto, amino and carboxyl radicals, heating said organic compound dissolved in said liquid body at a temperature between 100° and 500° C. at which said compound carbonizes therein until a finely dispersed carbonization product is formed and until said impurities are taken up by said carbonization product, and separating purified metal chloride from said carbonization product holding said impurities.

8. A continuous process for removing coloring impurities from an impure liquid chloride of a metal of group 4 of the periodic system, which comprises continually flowing into a reaction zone said chloride and a relatively small amount of an organic compound from the group consisting of hydrocarbons and compounds of carbon, hydrogen and at least one substituent from the group consisting of hydroxy, oxy, keto, amino and carboxyl radicals, continuously heating said organic compound in a liquid body of said chloride at a temperature between 100° and 500° C. at which said compound carbonizes therein until a finely dispersed carbonization product is formed and until said impurities are taken up by said carbonization product, continually removing from said zone said carbonization product holding said impurities and continually removing from said zone purified chloride of said metal.

9. A process as described in claim 8, the inflow

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to said zone being a stream of a solution of said compound in the impure liquid chloride.

10. A continuous process for removing coloring impurities from an impure liquid chloride of a metal of group 4 of the periodic system, which comprises continually flowing into a reaction zone said chloride and a relatively small amount of an organic compound from the group consisting of hydrocarbons and compounds of carbon, hydrogen and at least one substituent from the group consisting of hydroxy, oxy, keto, amino and carboxyl radicals, continuously heating said organic compound in a liquid body of said chloride in said zone at a temperature between 100° and 500° C. at which said compound carbonizes therein until a finely dispersed carbonization product is formed and until said impurities are taken up by said carbonization product, continuously distilling purified chloride of said metal from said zone, continually withdrawing part of the liquid therefrom, and separating purified metal chloride from the carbonization product in the withdrawn liquid holding the impurities.

11. A process for removing coloring impurities from liquid titanium tetrachloride which comprises intermixing said chloride and a small proportion of an organic compound selected from the group consisting of hydrocarbons and compounds of carbon, hydrogen and at least one substituent from the group consisting of hydroxy, oxy, keto, amino and carboxyl radicals, heating said organic compound in a liquid body of the titanium tetrachloride at a temperature between 100° and 500° C. at which said compound carbonizes therein until a finely dispersed carbonization product is formed and until said impurities are taken up by said carbonization product, and separating purified metal chloride from said carbonization product holding said impurities.

12. A process for removing coloring impurities from impure liquid titanium tetrachloride which comprises continually flowing into a reaction zone said titanium tetrachloride and a small proportion of an organic compound selected from the group consisting of hydrocarbons and compounds of carbon, hydrogen and at least one substituent from the group consisting of hydroxy, oxy, keto, amino and carboxyl radicals, continuously heating said organic compound in a liquid body of the titanium tetrachloride at a temperature between 100° and 500° C. at which said compound carbonizes therein until a finely dispersed carbonization product is formed and until said impurities are taken up by said carbonization product, continually removing from said zone said carbonization product holding said impurities, and continually removing from said zone purified chloride of said metal.

WALTER FREY.  
ERNST BOLLER.

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The following references are of record in the file of this patent:

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Ex parte RUBIN

Patent Office Board of Appeals

Opinion dated Sept. 30, 1959

United States Patents Quarterly Headnotes

#### PATENTS

##### [1] Affidavits - Anticipating references (§ 12.3)

##### Double patenting--In general (§ 33.1)

If applicant's claims are rejected as not patentable over claims of his prior patent, a Rule 131 affidavit is ineffective, as only one patent can issue for a single inventive concept; if applicant's claims are patentably distinct over those of the patent, a Rule 131 affidavit would not be required; therefore, there is no need for Board to consider affidavit.

#### PATENTS

##### [2] Abandonment--Disclosure without claiming (§ 10.7)

Basic requisite for rejection on ground that applicant dedicated claimed method to the public is that what is claimed in application is disclosed but not claimed in applicant's patent.

#### PATENTS

##### [3] Patentability - Change - In general (§ 51.251)

Same product is obtained by either method claimed in application or that claimed in applicant's prior patent; no unexpected result is obtained by reversing order of steps recited in method claimed in patent; hence, method claimed in application is not patentable over patented method.

#### PATENTS

##### Particular patents--Coated Sheet

Rubin, Method of Manufacturing a Conductive Coated Sheet, claims 2, 3, and 6 to 9 of application refused.

\*440 Appeal from Primary Examiner.

Application for patent, Serial No. 513,642. From decision rejecting claims 1 to 9, applicant appeals. Appeal dismissed as to claims 1, 4, and 5; affirmed as to claims 2, 3, and 6 to 9.

EZEKIEL WOLF, Boston, Mass., for applicant.

Before SURLE, Examiner in Chief, and MAGIL and WILES, Acting Examiners in Chief.

WILES, Acting Examiner in Chief.

This is an appeal from the final rejection of claims 1 to 9. Since claims 1, 4 and 5 were withdrawn from further consideration as not reading on the elected species, the appeal as to these claims will be dismissed, leaving for our consideration only claims 2, 3 and 6 to 9. No claims have been allowed.

\*441 Claims 2 and 9 are sufficiently representative and are reproduced below:

2. A method of manufacturing a plate or sheet having an electrical conductive non-alkali metallic plated coating which comprises taking a base sheet of flexible impregnable paper material, first impregnating the sheet from at least one side with a thermosetting resin and partially curing said resin in the sheet, then depositing a smooth highly-conductive metallic film of uniform thickness on the other side capable of being etched into a printed circuit, and then laminating the sheet to a backing sheet of thermosetting material and making the final cure of the assembly under heat and pressure.

9. A method of manufacturing a plate or sheet having an electrical conductive nonalkali metallic plated coating including the steps of taking a base sheet of flexible impregnable paper material and first impregnating the sheet from one side with a thermosetting resin, and the additional steps of depositing a smooth metallic film of uniform thickness and capable of being etched into a printed circuit on the other side of the base sheet, and laminating the sheet with the metallic coating and the resin to a backing sheet of thermosetting material, with the backing sheet on the side of the base sheet opposite the metallic film.

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The references relied upon are:

Baekeland, 1,019,406, March 5, 1912.

Keller, 2,439,137, April 6, 1948.

Rubin, 2,680,699, June 8, 1954.

The claims are directed to a method of forming a laminated sheet, one surface of which is made of highly conductive material, which method is more fully described on pages 3 to 5 of appellant's brief.

The alleged invention of the instant application is best summarized by appellant on page 5 of his brief as relating "to a method of making a laminated sheet wherein a base sheet is *first impregnated* with a thermosetting material and thereafter *coated* with a metallic film."

The examiner has rejected the claims as unpatentable over Rubin as well as unpatentable over Keller in view of Baekeland.

[1] As pointed out by appellant in his brief, the examiner several times seems to have considered appellant's patent as a publication, as he has rejected the appealed claims as unpatentable over the disclosure thereof, although in Paper No. 9, as well as in the statement, the rejection seems to be based upon the claims of the Rubin patent. The examiner has also expressed the view that a Rule 131 affidavit is ineffective for appellant to overcome his own patent if the present claims are unpatentable over the patent, and this view would imply, as more fully brought out by the examiner in answering appellant's arguments, that the basis for the rejection is the invention claimed in appellant's prior patent. In such a rejection if the appealed claims are not patentable over the claims of the patent, a Rule 131 affidavit obviously is ineffective, as only one patent can issue for a single inventive concept. However, if the claims herein are patentably distinct over those of the patent, a Rule 131 affidavit obviously would not be required. There is therefore no need to consider the Rule 131 affidavit.

[2] The examiner in his refusal of the claims has included in his statement language indicative that

he considers appellant to have dedicated to the public the method recited in the appealed claims. A basic requisite for a rejection on this ground is that what is claimed herein is disclosed but not claimed in appellant's patent. However, the examiner has not even alleged that the sequence of steps required by the claims before us is disclosed in the patent, and we fail to find any such disclosure in the patent. In fact, the examiner's argument as to the non-criticality of the reversal of the order of steps of the present claims over those of the Rubin patent indicates the lack of any such unclaimed disclosure in the patent. It is obvious therefore that there is no basis for any "dedication" of the method claimed herein and hence the position of the examiner is untenable and cannot be sustained. Ex parte Harman, Patent File No. 2,520,280, 86 USPO 487.

[3] This leaves for our consideration the question of whether the method claimed herein is patentable over the method claimed in appellant's patent as only one patent can be granted if there be but one invention. The examiner has quite fully set forth his position in support of this rejection and answered appellant's arguments with respect thereto. We therefore find little need for any extended comments except to note that appellant has not attempted to refute the examiner's position that it is not inventive to change the order of steps. In fact, appellant concedes that the same product is obtained by either the method claimed herein or that claimed in the patent. Moreover, appellant, on page 6 of the brief, states that:

"The method described in the patent is considered the better of the two \*442 methods invented, but the method set forth in the instant case does perform satisfactorily."

It is evident therefore that no unexpected result is obtained by reversing the order of steps recited in the method claimed in the Rubin patent. In re Haller et al., 24 CCPA 887, 1937 C.D. 281, 481 O.G. 6, 87 F.2d 520, 32 USPO 306; New Wrinkle, Inc., et al. v. Watson, 1953 C.D. 18, 670 O.G. 306, 204 F.2d 35, 96 USPO 436, 438. Accordingly, we agree with the examiner that the method recited in the appealed claims is not patentable over appellant's patented method and we will sustain the rejection.

The examiner has also rejected the claimed method

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as unpatentable over Keller in view of Baekeland, his position being as follows:

"Keller discloses impregnating a fibrous sheet with thermosetting resin and spraying a highly conductive metal on one or both sides of the sheet and laminating this to another similar resin impregnated sheet under heat and pressure. The Baekeland reference is used to show that curing a resin in several stages is old in the art. Partially curing the resin of Keller before the metal layer has been deposited is considered an obvious modification of Keller's process of curing. No invention is seen in applying a metal film of uniform thickness instead of the irregular thickness as in Keller since to do so would be mere mechanical expedient. Nowhere does applicant show the criticality of this step or that any new and unobvious result would be accomplished by coating the metal uniformly instead of non-uniformly."

While Keller discloses that the metal coating may be on one or both sides of the sheet, we find no disclosure therein which even suggests, when only one side is metallized, that the other side is to be impregnated with the thermosetting resin and that the impregnated side may then be laminated to a backing sheet of thermosetting material. Additionally, in the process of Keller it is the metallized face or side of the sheet which is laminated to a resinous material and results in a product which would not be suitable for appellant's purpose. We therefore are constrained to agree with appellant that the procedure of Keller is not suggestive of the claimed method and the rejection will not be sustained.

The appeal is dismissed as to claims 1, 4 and 5.

The decision of the examiner is affirmed.

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END OF DOCUMENT

Westlaw

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**In re BURHANS**

Court of Customs and Patent Appeals

Appl. No. 5128

Decided Apr. 1, 1946

United States Patents Quarterly Headnotes

**PATENTS****[1] Patentability--Aggregation or combination--In general**

Contention, that references do not teach applicant's steps which are new in art and necessary to obtain desired result, has no merit in absence of proof in record that order of performing steps produces new and unexpected results.

**PATENTS****Particular patents--Flour**

Burhans, Enriched and Whole Wheat Flour and Bread, claims 2, 4, 5, 6, 8, and 10 of application refused.

\*330 Appeal from Board of Appeals of the Patent Office.

Application for patent of Merton E. Burhans, Serial No. 401,968; Patent Office Division 63. From decision rejecting claims 2, 4, 5, 6, 8, and 10, applicant appeals. Affirmed.

JOHN F. EAKINS, Chicago, Ill., for appellant.

W. W. COCHRAN (E. L. REYNOLDS of counsel)  
for the Commissioner of Patents.

O'CONNELL, Judge.

This is an appeal from the decision of the Board of Appeals of the United States Patent Office affirming the action of the Primary Examiner in rejecting in appellant's application for a patent claims 2 and 4 for a method of making flour, claims 5 and 6 for a method of making bread, and claims 8 and 10 for an article of manufacture of genuine whole wheat flour.

The foregoing claims were all rejected as lacking invention over the prior art and claims 5 and 6 were further rejected as aggregative. There were no claims allowed.

Claims 4, 6, and 10 are illustrative and sufficiently descriptive of the alleged invention. They read:

4. The method of making genuine whole wheat flour which consists in separating the germs from the wheat, manufacturing flour from the remaining constituents of the wheat, aging the flour, incorporating therein finely divided non-rancid wheat germ constituents, and thereafter impregnating the flour with carbon dioxide.

6. The method of making genuine whole wheat bread which consists in separating germ constituents from wheat, reducing the remaining constituents of the wheat to flour, aging the flour, incorporating in the aged flour finely divided non-rancid wheat germ constituents, thereafter impregnating the flour with carbon dioxide, making the flour into dough and baking the dough while the flour still retains a substantial amount of carbon dioxide.

10. As an article of manufacture, genuine whole wheat flour comprising finely divided non-rancid wheat germ constituents and the remaining constituents of the wheat in finely divided and aged condition, the whole mass of the flour being impregnated with carbon dioxide.

The references are:

Currie (Br.) 5,614 of 1828

Byrne 29,859 Sept. 4, 1860

Dietz 1,974,808 Sept. 25, 1934

Donk et al. 2,085,421 June 29, 1937

Wellingtonhoff 2,230,417 Feb. 4, 1941

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In support of his position here, appellant states in his brief:

\*331 \* \* \* It is pertinent to note that the reason that white bread is so widely used notwithstanding its well-known deficiencies, is that flour to be used by bakers must be aged before it acquires good baking qualities. The aging of flour is an oxidation process which can be effected by allowing the air to work on the flour for an adequate period of time. It was found that flour could be aged much more rapidly by incorporating therein an oxidizing agent and flour thus aged is usually referred to as "patent" flour. The wheat germ contains a large proportion of oil and this oil has a great tendency to become rancid. To avoid this rancidity the milling art has from time immemorial separated the germ from the wheat and the resulting flour could then be aged. The development of rancidity is also an oxidation process and if the germ were ground up with the wheat kernel the aging process would inevitably result in full development of rancidity.

The present applicant has discovered that carbon dioxide has the quality of preventing overaging of flour and of preventing the development of rancidity. Consequently his method of making a true whole wheat flour or an enriched flour comprises the following steps in the order stated:

*a. separating the germs from the wheat kernels and the manufacture of flour from the rest of the kernel;*

*b. aging the germless flour;*

*c. incorporating in the aged germless flour finely divided non-rancid wheat germ constituents; and*

*d. impregnating the flour with carbon dioxide.*  
(Emphasis quoted)

The appealed claims have all been rejected on Donk et al., Wellinghoff and Dietz in view of Byrne or Currie.

Currie shows a method of preserving grain and other vegetable and animal substances by the application of

carbon dioxide while the material is stored in air-tight vessels, or other proper receptacles. He thus prevents, according to his disclosure, the tendency of the grain to vegetate and greatly hinders the decomposition of other vegetable and animal matters.

Byrne discloses a process for treating the flour of wheat and other grain with carbon dioxide while the flour is inclosed in an ordinary flour bolting chest. In his specification, Byrne states--

It is a well known fact to dealers in flour, that the flour of wheat when freshly ground is unfit for the use of bakers, as it makes a much smaller loaf than when it has acquired some age. It is also well known that too much age causes decomposition, the flour generates animalcules and becomes unfit for any use except starch manufacture. As a remedy for these evils, I treat freshly ground flour with carbonic acid gas. It renders fresh flour fit for immediate use and prevents flour at a far advanced age from decomposition.

In the patent to Dietz it is pointed out that "the introduction of the wheat germ, as such, into flour tends, by reason of the relatively large quantity of germ oil, to make the flour rancid and to affect its color and texture." Dietz describes "a process for making flour by extracting the germ from the wheat, milling the residue into flour, extracting and activating the oil from the germ "to a high potency in vitamin D and the activated oil is then mixed with the residue of the germ in any desired proportion." The resultant mixture is then introduced in small quantities into flour prepared in any usual manner.

Donk et al. relates to processes in treating wheat germ so as to make it useful in the manufacture of bakery and other food products. The patentee separately grinds and treats the fresh wheat germ as released in the flour mill in the process of milling. It is then packaged in appropriate containers in an inert gas such as carbon dioxide. Subsequently the treated wheat germ is incorporated into bakers' mixture. To cure the deficiency in refined wheat flour as ordinarily used for bread, one of the principal objects of Donk et al. is "to make available for introduction into the ordinary bakers' mixture for bread an even larger proportion of wheat germ than is ordinarily in the wheat grain or berry."



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Wellinghoff removes the oil from the wheat germ and the non-rancid residue is reintroduced into the flour stream for further milling with the flour.

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Dietz, Wellinghoff and Donk et al. do not specifically describe the step of aging the flour, but it is referred to in Byrne and each of the foregoing references contemplate that the flour would be aged prior to its use by the baker. The aging of flour is not only old in the art but it is also conventional as hereinbefore noted. In Dietz, Wellinghoff and Donk et al. the wheat germ is separately ground and treated to remove the rancid element in the germ and the non-rancid germ is thereafter incorporated in aged flour for the bakers' mixture. Donk et al. also shows that rancidity may be eliminated by storing the germ contents in carbon dioxide, and Byrne discloses \*332 that it is old to impregnate flour with carbon dioxide for the purpose not only of rendering freshly ground flour fit for immediate use by the baker but also of preserving the flour by the prevention of its decomposition.

END OF DOCUMENT

The cited references considered collectively clearly suggest doing the thing that appellant has done in this case and the Primary Examiner and the Board of Appeals correctly decided that the methods and article defined in the appealed claims were not patentable over the art of record for the reason that what appellant has done would be obvious to anyone skilled in the art. See In re Stover, 32 C.C.P.A. (Patents) 823, 146 F.2d 299, 64 USPO 186.

[1] Appellant contends that the references taken singly or together do not teach his characteristic four steps which are new in the art and which are necessary to obtain the desired result. There is no merit in the point here in the absence of any proof in the record that the order of performing the steps produces any new and unexpected results. See In re Gibson, 17 C.C.P.A. (Patents) 1090, 39 F.2d 975, 5 USPO 230; In re Lang et al., 25 C.C.P.A. (Patents) 1322, 97 F.2d 626, 38 USPO 187; In re McKee, 23 C.C.P.A. (Patents) 1187, 83 F.2d 819, 29 USPO 493.

In view of our conclusion it is unnecessary to discuss and pass upon the question of aggregation and the decision of the Board of Appeals is accordingly affirmed.